# LIQUEFACTION OF NOVA SCOTIA COALS
# PHASE IV

## STUDIES ON HIGH PRESSURE DONOR SOLVENT LIQUEFACTION AND CATALYTIC HYDROGENATION OF SYDNEY AREA COALS

FINAL REPORT

**Nova Scotia Research Foundation Corporation**
Dartmouth, Nova Scotia

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by

NOVA SCOTIA RESEARCH FOUNDATION CORPORATION

Prepared by

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TABLE OF CONTENTS


| | | PAGE |
|---|---|---|
| ACKNOWLEDGMENTS | | vi |
| SUMMARY | | vii |
| INTRODUCTION | | 1 |
| TASK 1 - | PREPARATION AND ANALYSIS OF MATERIALS | 4 |
| 1.1 | Coal Feedstocks | 4 |
| 1.2 | Anthracene Oil | 8 |
| 1.3 | Catalysts | 11 |
| TASK 2 - | HYDROGENATION OF ANTHRACENE OIL | 13 |
| TASK 3 - | CATALYST SCREENING TESTS | 20 |
| 3.1 | Procedures | 21 |
| 3.2 | Results and Discussion | 24 |
| TASK 4 - | LITERATURE REVIEW: SEPARATION AND CHARACTERIZATION OF COAL LIQUIDS | 34 |
| 4.1 | Introduction | 34 |
| 4.2 | Separation Methods | 35 |
| 4.3 | Characterization Methods | 47 |
| TASK 5 - | INSTALLATION AND OPERATION OF NEW EQUIPMENT | 53 |
| 5.1 | Description of Continuous Coal Liquefaction Unit | 55 |
| 5.2 | Results of Preliminary Trials | 57 |
| TASK 6 - | CONTINUOUS DONOR SOLVENT LIQUEFACTION OF SYDNEY AREA COALS | 61 |
| 6.1 | Coal Hydrogenation Parameter Study | 61 |
| 6.2 | Dependence of Liquefaction Behavior on Coal Properties | 67 |
| 6.3 | Recovery of Coal Liquids | 77 |
| 6.4 | Mechanisms of Hydrogen Transfer in Donor Solvent Liquefaction of Coal | 82 |
| CONCLUSIONS AND RECOMMENDATIONS | | 87 |
| REFERENCES | | 92 |

TABLE OF CONTENTS (Continued)

APPENDICES


| | | PAGE |
|---|---|---|
| APPENDIX A - | CONVERSION CALCULATIONS | A-1 |
| APPENDIX B - | SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS | B-1 |
| APPENDIX C - | MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS | C-1 |
| APPENDIX D - | ANALYSIS OF BENZENE SOLUBLE FRACTIONS FROM CONTINUOUS COAL LIQUEFACTION TESTS | D-1 |
| APPENDIX E - | STATISTICAL ANALYSIS OF $2^4$ FACTORIAL EXPERIMENT ON LINGAN AND PRINCE MINE COALS | E-1 |
| APPENDIX F - | PRELIMINARY RESULTS OF HPLC APPLIED TO COAL-DERIVED LIQUIDS | F-1 |
| APPENDIX G - | OPERATING PROCEDURE FOR CONTINUOUS COAL LIQUEFACTION UNIT | G-1 |
| APPENDIX H - | AUTOMATED HIGH PRESSURE LETDOWN SYSTEM | H-1 |
| APPENDIX I - | EQUIPMENT FOR CONTINUOUS COAL LIQUEFACTION UNIT | I-1 |

TABLE OF CONTENTS (Continued)


| NO. | TABLES | PAGE |
|---|---|---|
| 1. | Analysis of Coals Tested | 5 |
| 2. | Petrographic Characteristics of Coals Tested | 7 |
| 3. | Analysis of Raw Anthracene Oil | 9 |
| 4. | Chemical and Physical Properties of Hydrotreating Catalysts | 12 |
| 5. | Reaction Conditions for Anthracene Oil Hydrogenation | 14 |
| 6. | Characteristics of Hydrogenated Anthracene Oil | 15 |
| 7. | Analysis of 20-Liter Batches of 9% H Solvent | 19 |
| 8. | Batch Autoclave Results for Lingan Coal in Thermal and Catalytic Modes of Operation | 25 |
| 9. | Results of Batch Autoclave Catalyst Screening Tests | 27 |
| 10. | Simulated Distillation of Benzene-Soluble Fractions from Catalyst Screening Tests | 29 |
| 11. | Elemental Analysis on Pentane and Benzene Solubles from Catalyst Screening Tests | 31 |
| 12. | Results of Preliminary Continuous Coal Liquefaction Trials | 59 |
| 13. | Summary of Results from Coal Hydrogenation Parameter Study Using Continuous-Flow Unit | 64 |
| 14. | Product Distributions from Continuous Experiments With Prince, Lingan and No. 26 Colliery Coals | 68 |
| 15. | Results of Batch Vacuum Distillation/Coking Experiments | 80 |
| 16. | Analysis of Pentane-Soluble Fractions from Continuous Coal Liquefaction Tests | 81 |
| 17. | Proton Distributions for Raw and Hydrogenated Anthracene Oil | 84 |
| 18. | H-NMR Analysis of Various Liquefaction Product Fractions | 85 |

TABLE OF CONTENTS (Continued)


| NO. | FIGURES | PAGE |
|---|---|---|
| 1. | H-NMR Spectra of Raw Anthracene Oil with 5.70 Wt. % Hydrogen | 10 |
| 2. | A Comparison of ASTM Distillations (D-1160) for Raw and Hydrogenated Anthracene Oil | 16 |
| 3. | H-NMR Spectra of Hydrogenated Anthracene Oil with 7.64 Wt. % Hydrogen | 17 |
| 4. | H-NMR Spectra of Hydrogenated Anthracene Oil with 9.05 Wt. % Hydrogen | 18 |
| 5. | Schematic Diagram of High Pressure Autoclave System | 22 |
| 6. | Influence of Catalysts on Conversion of Lingan Coal at 450°C | 28 |
| 7. | Flowsheet for Continuous Coal Liquefaction Unit | 56 |
| 8. | Effect of Temperature on Conversion of Lingan Coal | 60 |
| 9. | Influence of Pyritic Sulphur Content on Coal Conversion | 70 |
| 10. | Coal Conversion as a Function of Organic Sulphur Content | 71 |
| 11. | Variation of Coal Conversion with Total Sulphur Content | 72 |
| 12. | Effect of Ash Content on Coal Conversion | 73 |
| 13. | Influence of Carbon Content on Coal Conversion | 74 |
| 14. | Variation of Coal Conversion with Vitrinite Content | 75 |
| 15. | Effect of Rank on Coal Conversion | 76 |
| 16. | Simplified Flow Diagram of Vacuum Distillation/Coking Apparatus | 79 |
| 17. | HPLC Separation of Hydrogenated Anthracene Oil | F-3 |
| 18. | Molecular Weight Distribution of Hydrogenated Anthracene Oil by GPC | F-5 |

TABLE OF CONTENTS (Continued)


| NO. | FIGURES | PAGE |
|---|---|---|
| 19. | Molecular Weight Distribution of THF-Soluble Fraction from Run No. 3115 | F-6 |
| 20. | Molecular Weight Distribution of THF-Soluble Fraction from Run No. 3116 | F-7 |

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## SUMMARY

The fourth phase of an experimental program on the direct liquefaction of Nova Scotia coal has been completed. This phase of work was concentrated on high severity donor solvent liquefaction and catalytic hydrogenation of Sydney area coals. A total of ten coal samples from three operating mines in Cape Breton have been tested. I addition, analytical methods for the separation and characterization of coal-derived liquids have been reviewed.

During Phase IV our continuous coal liquefaction unit has been extensively modified and upgraded. Continuous donor solvent liquefaction runs were carried out with Lingan, Prince and No. 26 Colliery coals in a once-through mode of operation. Hydrogenated anthracene oil, 9 wt. % H, was used as donor vehicle. These experiments have shown that coal feedstock, reaction temperature and coal space velocity affect product composition. Furthermore, it has been shown that Hub seam coal from the Prince mine is the most reactive feedstock at thermal liquefaction conditions. Within the Harbour seam reactivity was observed to decrease in going from the Lingan mine to No. 26. At high severity operating conditions, 460°C and 20.68 MPa, conversions for these coals ranged from 85 - 89% while oil yield ranged from 20 - 34%. Simple correlations have been drawn between individual coal properties, both chemical and petrographic, and product yields.

Batch autoclave experiments have shown that catalytic hydrogenation produces higher oil yields than donor solvent extraction. This is primarily attributed to the fact that the catalyst promotes chemical consumption of molecular hydrogen. In high severity experiments with Lingan coal and hydrogenated anthracene oil containing 7.6 wt. % H, oil yield was typically 26%. The addition of commercial Co/Mo and Ni/Mo hydrotreating catalysts increased oil yield to about 37%. The highest oil yield, 49%, was achieved using a mixture containing Ni, Mo and Sn.

The next phase of work will concentrate on conventional single-stage catalytic hydrogenation and two-stage thermal/catalytic liquefaction. In regard to single-stage catalytic hydrogenation, we plan to carry out continuous experiments with solvent recycle. The two-stage process will be comprised of a thermal first step to solubilize the coal followed by a catalytic second step to stabilize the first-stage effluent while producing a recycle oil with high donor capacity.

## INTRODUCTION

During the past decade several industrialized countries around the world, including Canada, have focused considerable attention on the production of liquid fuels from coal. The search for alternate sources of liquid fuels has been stimulated by the upward trend in crude oil prices and a delicate supply/demand balance for petroleum products. Although Canada has abundant coal reserves, the Canadian Government has not made a commitment to developing a coal liquefaction process because of the enormous costs involved. On the other hand, the Canadian way of life is highly dependent on petroleum liquids. Since our existing crude supplies are not expected to meet our future liquid fuel demands it seems that we will have to rely on synthetic liquid fuels to some degree in the next few decades.

Currently the EDS, H-Coal and Ruhrkohle/Veba processes are at advanced stages of development while synthetic liquid fuels are being produced commercially by Fisher-Tropsch synthesis. Since long lead times are involved in process evaluation, detailed design and plant construction it is essential to understand the basic concepts of the promising liquefaction processes and verify their projected yield structures as they apply to Canadian coals.

Process studies relating to the direct liquefaction of Nova Scotia coals were initiated at the Nova Scotia Research Foundation Corporation in the latter part of 1977. Since that time four phases of

our research program have been completed. Yield data has been developed over a wide range of operating conditions. The product slate of interest in Nova Scotia is liquid transportation fuels. Thus research efforts are being directed towards identifying or developing a process configuration to maximize the yield of coal-derived liquids.

The first and second phases of our program were concentrated on producing liquids via low severity extraction-coking (1, 2, 3). In this approach hydrogen donor solvent is used under mild conditions (<2100 kPa, 400$^{o}$C) to extract the coal followed by delayed coking as a product separation step. Although the low pressure extraction has advantages related to plant hardware there is one major disadvantage, liquid yield is low. Experimental work showed that for one hour extractions conversions of Lingan coal to benzene solubles plus gases were typically 60%. However, following the coking step liquid yield was 30 wt. %. A variety of methods were investigated to enhance liquid yield from the process but results obtained were not encouraging. Hence it was decided to abandon the low severity approach in pursuit of higher yields of liquid products.

Phases III and IV of the project have been concentrated on medium to high pressure donor solvent liquefaction and catalytic hydrogenation. During Phase III donor solvent extraction experiments were conducted in our high pressure batch system (4). The effects of temperature, pressure, time and solvent/coal ratio were investigated. Yields of oil, asphaltenes, preasphaltenes and gases were determined. Conver-

sion of Lingan coal increased from 60 to 80 wt. % at higher severity operating conditions; 20.68 MPa, 450°C. In Phase IV several materials considered to be promising hydroliquefaction catalysts were tested. The results of the catalyst screening experiments are presented in Task 3.

Construction of the first version of our continuous-flow coal liquefaction unit was completed in 1980. During the commissioning trials it was observed that solids sedimentation occurred in the up-flow tubular reactor. Consequently, long on-stream periods would be required to reach steady state operating conditions. Since our intention was to conduct experiments of relatively short duration, 6-12 hours, it was decided to replace the tubular reactor with a stirred tank reactor.

During the period July, 1981 to October, 1982 the continuous system was modified and upgraded extensively. Design changes were implemented and equipment was added to the unit in order to improve operability and mass balance closures. The system is presently suitable for processing up to 3 Kg per hour of coal-oil slurry. A detailed description of the unit is given herein.

Continuous donor solvent liquefaction experiments began in June of 1982. Since that time ten coals from three operating mines in Cape Breton have been tested. Within recent months emphasis has been placed on the petrographic characteristics of the coal feedstocks. Details pertaining to operations and product yields are presented in this report.

## TASK 1 - PREPARATION AND ANALYSIS OF MATERIALS

### 1.1 Coal Feedstocks

Ten coal feedstocks were tested during this phase of the project. The coals were channel samples from three operating mines in Cape Breton - Lingan, Prince and No. 26. These coal samples were provided courtesy of the Cape Breton Development Corporation. Preparation involved riffling, grinding and screening. After screening, the individual coals were thoroughly mixed and stored in plastic-lined drums with a nitrogen blanket.

Proximate and ultimate analysis of the coals used are given in Table 1. Proximate analysis, free swelling index and forms of sulphur were determined according to standard methods. Total sulphur was measured using a Leco sulphur analyzer. Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer elemental analyzer.

Petrographic analyses of six coals are given in Table 2. These analyses were carried out by the coal petrology unit at the Bedford Institute of Oceanography.

TABLE 1

ANALYSIS OF COALS TESTED

| COAL DESCRIPTION: | LINGAN BATCH E | LINGAN BATCH F | LINGAN BATCH G | LINGAN BATCH I | LINGAN BATCH J |
|---|---|---|---|---|---|
| Moisture, Wt. % | 1.68 | 1.37 | 1.36 | 1.39 | 1.47 |
| PROXIMATE (Dry Basis) Wt. % | | | | | |
| Ash | 3.28 | 7.09 | 3.13 | 2.82 | 6.37 |
| Volatile Matter | 34.42 | 36.24 | 34.57 | 38.14 | 37.02 |
| ULTIMATE (Dry Basis) Wt. % | | | | | |
| Carbon | 80.50 | 77.90 | 81.71 | 81.40 | 78.84 |
| Hydrogen | 5.22 | 5.27 | 5.37 | 5.34 | 5.00 |
| Nitrogen | 1.89 | 1.74 | 1.87 | 1.63 | 1.62 |
| Sulphur | 0.96 | 3.60 | 0.91 | 1.00 | 2.69 |
| Ash | 3.28 | 7.09 | 3.13 | 2.83 | 6.37 |
| Oxygen (by difference) | 8.15 | 4.40 | 7.01 | 7.80 | 5.48 |
| SULPHUR FORMS (Dry Basis) Wt. % | | | | | |
| Sulphate | <0.01 | 0.47 | <0.01 | 0.06 | 0.07 |
| Pyritic | 0.63 | 2.63 | 0.61 | 0.54 | 1.87 |
| Organic (by difference) | 0.33 | 0.50 | 0.30 | 0.40 | 0.75 |
| Total | 0.96 | 3.60 | 0.91 | 1.00 | 2.69 |
| FREE SWELLING INDEX | - | - | - | 8 | 8 |

TABLE 1 (Continued)

ANALYSIS OF COALS TESTED

| COAL DESCRIPTION: | LINGAN BATCH K | PRINCE BATCH B | PRINCE BATCH C | PRINCE BATCH D | NO. 26 BATCH B |
|---|---|---|---|---|---|
| MOISTURE, Wt. % | 1.23 | 1.80 | 2.43 | 1.98 | 0.88 |
| PROXIMATE (Dry Basis) Wt. % | | | | | |
| Ash | 3.89 | 17.07 | 6.42 | 9.23 | 4.00 |
| Volatile Matter | 37.36 | 32.86 | 36.54 | 36.22 | 34.60 |
| ULTIMATE (Dry Basis) Wt. % | | | | | |
| Carbon | 81.47 | 60.91 | 77.23 | 73.48 | 80.30 |
| Hydrogen | 5.06 | 4.19 | 4.86 | 4.80 | 5.20 |
| Nitrogen | 1.70 | 1.85 | 1.55 | 1.45 | 1.67 |
| Sulphur | 1.80 | 6.68 | 3.04 | 4.22 | 1.11 |
| Ash | 3.89 | 17.07 | 6.42 | 9.23 | 4.00 |
| Oxygen (by difference) | 6.08 | 9.03 | 6.90 | 6.82 | 7.72 |
| SULPHUR FORMS (Dry Basis) Wt. % | | | | | |
| Sulphate | 0.03 | 0.48 | 0.28 | 0.18 | 0.05 |
| Pyritic | 1.21 | 5.69 | 1.39 | 2.25 | 0.42 |
| Organic (by difference) | 0.56 | 0.51 | 1.37 | 1.79 | 0.64 |
| Total | 1.80 | 6.68 | 3.04 | 4.22 | 1.11 |
| FREE SWELLING INDEX | 8 | - | 2½ | 2 | 8 |

TABLE 2

PETROGRAPHIC CHARACTERISTICS OF COALS TESTED

| COAL DESCRIPTION: | LINGAN BATCH I | LINGAN BATCH J | LINGAN BATCH K | PRINCE BATCH C | PRINCE BATCH D | NO. 26 BATCH B |
|---|---|---|---|---|---|---|
| MACERAL COMPOSITION (% by Volume) | | | | | | |
| Vitrinite | 75.6 | 81.2 | 74.6 | 76.8 | 74.7 | 85.2 |
| Exinite | 6.2 | 5.3 | 7.4 | 3.1 | 4.1 | 3.2 |
| Inertinite | 18.0 | 9.9 | 17.4 | 18.5 | 18.0 | 11.2 |
| Macrinite | 2.8 | 1.5 | 1.6 | 1.4 | 0.8 | 1.8 |
| Micrinite | 6.2 | 1.7 | 4.4 | 5.9 | 5.4 | 3.6 |
| Semifusinite | 5.8 | 1.9 | 6.6 | 4.1 | 5.4 | 3.6 |
| Fusinite | 3.2 | 4.8 | 4.8 | 7.1 | 6.4 | 2.6 |
| Mineral Matter | 0.2 | 3.6 | 0.6 | 1.6 | 3.2 | 0.4 |
| Pyrite | 0.2 | 3.2 | 0.4 | 1.0 | 2.6 | 0.2 |
| Quartz | - - | - - | - - | - - | - - | 0.2 |
| Shale | - - | 0.2 | - - | 0.4 | 0.4 | - - |
| Calcite | - - | 0.2 | 0.2 | 0.2 | 0.2 | - - |
| % Ro Max. | 0.94 | 0.92 | 0.98 | 0.83 | 0.78 | 1.08 |

## 1.2 Anthracene Oil

This material is a coal-tar distillate which contains ca. 5.5 wt. % hydrogen. It was supplied by Domtar Chemicals Limited (Hamilton, Ontario). Hydrogenated solvents used in the batch and continuous coal hydrogenation experiments were prepared from this oil.

The characteristics of the raw oil are presented in Table 3. Carbon and hydrogen were determined using a Perkin-Elmer elemental analyzer. A standard Kjeldahl method was used for the determination of nitrogen. Total sulphur content was measured by X-ray fluorescence. The per cent of total hydrogen that occurs in different structural environments was determined by proton nuclear magnetic resonance (H-NMR). Figure 1 is a typical H-NMR spectrum of raw anthracene oil.

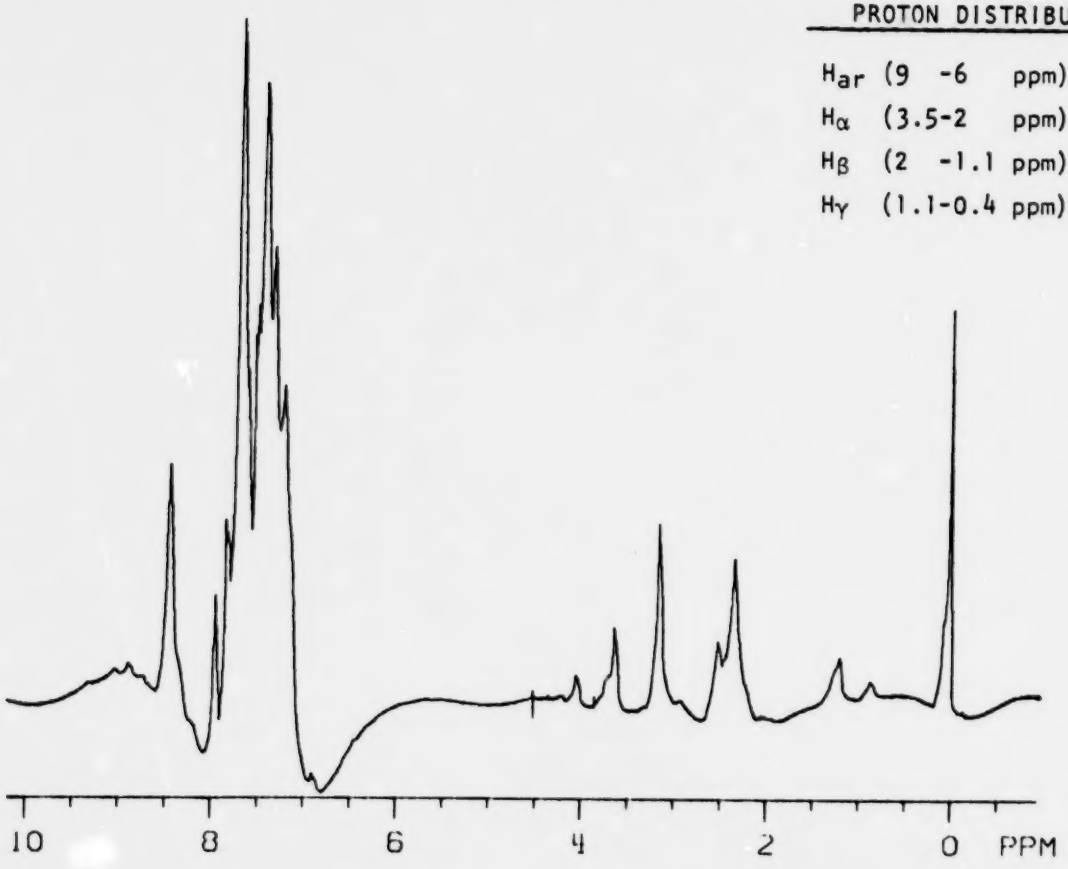
TABLE 3

ANALYSIS OF RAW ANTHRACENE OIL

| | |
|---|---|
| Specific Gravity, 60/60°F | 1.138 |
| Carbon, Wt. % | 90.70 |
| Hydrogen, Wt. % | 5.70 |
| Nitrogen, Wt. % | 0.96 |
| Sulphur, Wt. % | 0.73 |
| Proton Distribution, % | |
| $H_{ar}$ (9-6 ppm) | 89.22 |
| $H_{\alpha}$ (3.5 - 2 ppm) | 7.84 |
| $H_{\beta}$ (2 - 1.1 ppm) | 1.96 |
| $H_{\gamma}$ (1.1 - 0.4 ppm) | 0.98 |
| Distillation Data, °C (ASTM D-1160) | |
| IBP | 227 |
| 10% | 267 |
| 20% | 302 |
| 30% | 317 |
| 40% | 334 |
| 50% | 345 |
| 60% | 359 |
| 70% | 377 |
| 80% | 396 |
| 90% | 430 |
| 95% | 461 |
| EP | 471 |

Figure 1 H-NMR SPECTRA OF RAW ANTHRACENE OIL WITH 5.70 WT. % HYDROGEN

| PROTON DISTRIBUTION, % | |
|---|---|
| $H_{ar}$ (9 -6 ppm) | 89.22 |
| $H_{\alpha}$ (3.5-2 ppm) | 7.84 |
| $H_{\beta}$ (2 -1.1 ppm) | 1.96 |
| $H_{\gamma}$ (1.1-0.4 ppm) | 0.98 |



## 1.3 Catalysts

Twelve potential coal liquefaction catalysts were evaluated in the catalyst screening test program (Task 3). Compounds of iron, nickel, cobalt, molybdenum and tin were tested. All of the chemicals used were *certified grade* procured from commercial suppliers. Three commercial hydrotreating catalysts were included in this study. The chemical and physical properties of these Co/Mo and Ni/Mo catalysts are given in Table 4. This data was provided by the manufacturers.

TABLE 4

CHEMICAL AND PHYSICAL PROPERTIES OF HYDROTREATING CATALYSTS

| | NALCOMO 479 | HDS-1442 | NALCO NM502 |
|---|---|---|---|
| $MoO_3$, Wt. % | 19.0 | 13.2 | 14.0 |
| CoO, Wt. % | 4.4 | 3.5 | |
| NiO, Wt. % | | | 4.0 |
| Size, cm | 0.16 | 0.16 | 0.16 |
| Surface Area, $M^2/g$ | 180 | 300 | 240 |
| Pore Volume, cc/g | 0.47 | 0.69 | 0.53 |
| Density, g/cc | 0.82 - 0.84 | 0.60 | 0.73 - 0.74 |
| Crush Strength, Kg | 6.4 - 7.3 | | 6.4 - 7.3 |

Nalcomo 479 and Nalco NM502 are manufactured by the Nalco Chemical Company.

HDS-1442 is manufactured by American Cyanamid.

## TASK 2 - HYDROGENATION OF ANTHRACENE OIL

This task was an integral part of Phase IV. Solvents with varying hydrogen content were prepared from raw anthracene oil using a fixed-bed catalytic hydrotreater. The bench-scale unit has been described in an earlier report (3).

A commercial Co/Mo/Al hydrotreating catalyst, Nalcomo 479, was used to prepare solvents containing 6.4, 7.6 and 9.1% hydrogen. A summary of the operating conditions used to produce these solvents is given in Table 5. The characteristics of the three hydrogenated oils are shown in Table 6. A comparison of distillation data (ASTM D-1160) is presented in Figure 2. H-NMR spectra for the 7.6 and 9.1% H solvents are given in Figures 3 and 4.

The continuous donor solvent liquefaction experiments described in Task 6 required approximately 220 liters of 9% H solvent. This material was prepared at the rate of ca. 1.8 liters per 7 hour man-day. The hydrogenated oil so prepared was mixed to obtain 20-liter batches. Nine 20-liter batches were prepared during this phase of the project. Analysis of the individual batches are given in Table 7. Prior to starting the continuous experiments, 9% H solvent produced during Phase IV was blended with similar oil on hand at NSRFC. The analysis given in Table 6 is representative of the composite oil, used in the test program.

TABLE 5

REACTION CONDITIONS FOR ANTHRACENE OIL HYDROGENATION

| | | | |
|---|---|---|---|
| Reactor Temperature, $^{o}C$ | 362 | 367 | 373 |
| Reactor Pressure, MPa | 8.62 | 13.79 | 15.51 |
| LHSV | 1.05 | 0.80 | 0.22 |
| Hydrogen Flow, L/Hr | 12 | 55 | 60 - 120 |
| Product Hydrogen Content, Wt. % | 6.42 | 7.64 | 9.05 |

Catalyst used: Nalcomo 479.

TABLE 6

CHARACTERISTICS OF HYDROGENATED ANTHRACENE OIL

| SAMPLE DESCRIPTION | HAO 1 | HAO 2 | HAO 4 |
|---|---|---|---|
| Specific Gravity, 60/60°F | 1.105 | 1.068 | 1.029 |
| Carbon, Wt. % | 91.79 | 91.27 | 90.04 |
| Hydrogen, Wt. % | 6.42 | 7.64 | 9.05 |
| Nitrogen, Wt. % | 0.68 | 0.38 | 0.10 |
| Sulphur, Wt. % | 0.207 | 0.057 | 0.006 |
| Proton Distribution, % | | | |
| $H_{ar}$ (9-6 ppm) | 68.01 | 47.20 | 26.95 |
| $H_{\alpha}$ (3.5 - 2 ppm) | 20.16 | 23.20 | 24.11 |
| $H_{\beta}$ (2 - 1.1 ppm) | 9.91 | 21.60 | 38.30 |
| $H_{\gamma}$ (1.1 - 0.4 ppm) | 1.92 | 8.00 | 10.64 |
| Distillation Data, °C (ASTM D-1160) | | | |
| IBP | 200 | 188 | 179 |
| 10% | 258 | 251 | 251 |
| 20% | 290 | 280 | 273 |
| 30% | 307 | 299 | 291 |
| 40% | 321 | 312 | 303 |
| 50% | 332 | 324 | 312 |
| 60% | 344 | 334 | 322 |
| 70% | 357 | 346 | 334 |
| 80% | 374 | 366 | 353 |
| 90% | 393 | 392 | 379 |
| 95% | 416 | 414 | 402 |
| EP | 428 | 435 | 433 |

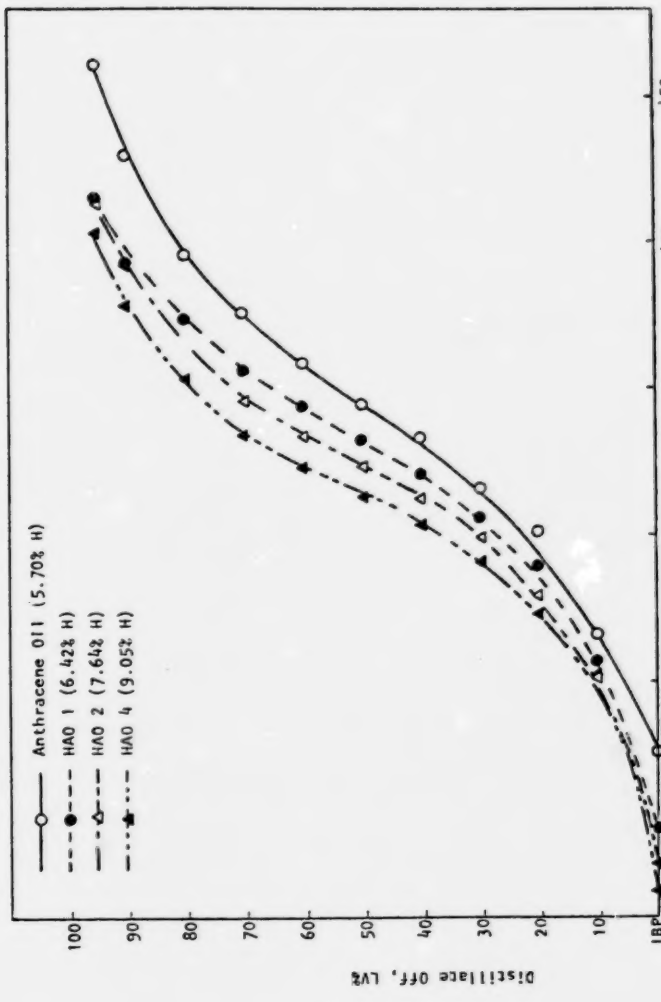



Figure 2 - A COMPARISON OF ASTM DISTILLATIONS (D-1160) FOR RAW AND HYDROGENATED ANTHRACENE OIL

Figure 3 H-NMR SPECTRA OF HYDROGENATED ANTHRACENE OIL WITH 7.64 WT. % HYDROGEN

| PROTON DISTRIBUTION, % | | |
|---|---|---|
| $H_{ar}$ | (9 -6 ppm) | 47.20 |
| $H_{\alpha}$ | (3.5-2 ppm) | 23.20 |
| $H_{\beta}$ | (2 -1.1 ppm) | 21.60 |
| $H_{\gamma}$ | (1.1-0.4 ppm) | 8.00 |

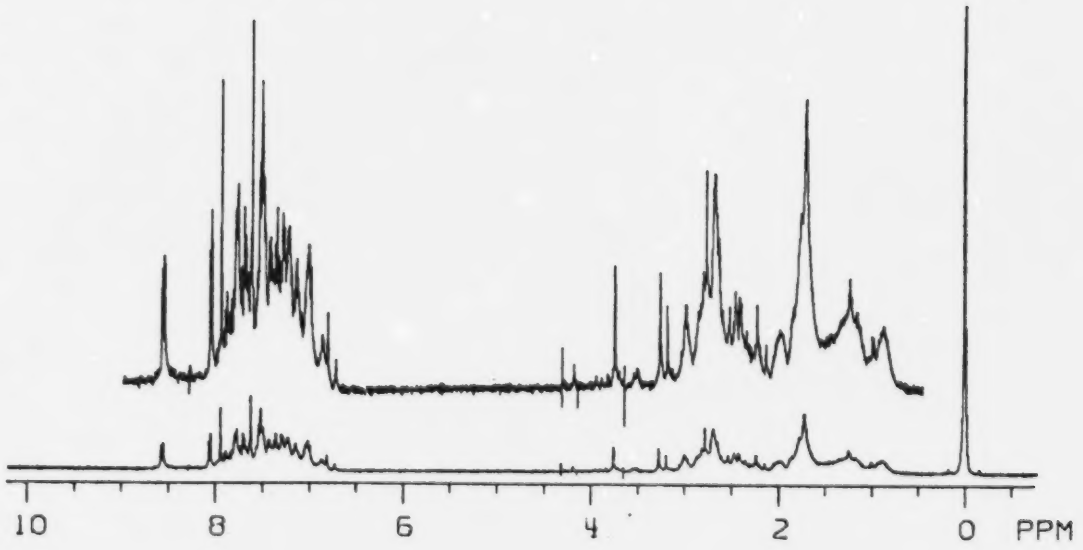


Figure 4 H-NMR SPECTRA OF HYDROGENATED ANTHRACENE OIL WITH 9.05 WT. % HYDROGEN

| PROTON DISTRIBUTION, % | | |
|---|---|---|
| $H_{ar}$ | (9 -6 ppm) | 26.95 |
| $H_{\alpha}$ | (3.5-2 ppm) | 24.11 |
| $H_{\beta}$ | (2 -1.1 ppm) | 38.30 |
| $H_{\gamma}$ | (1.1-0.4 ppm) | 10.64 |

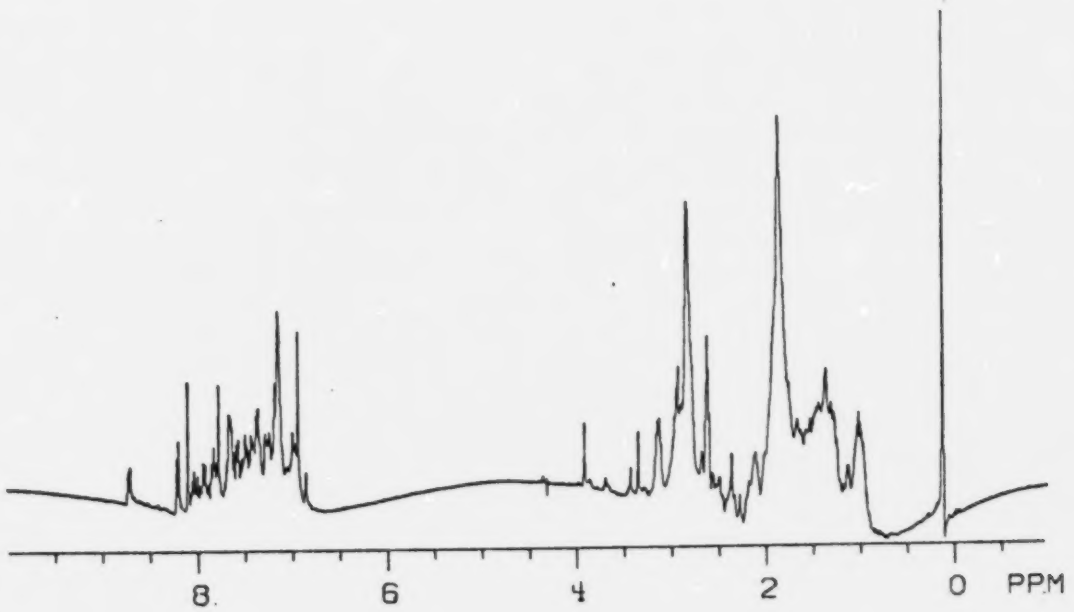


TABLE 7

ANALYSIS OF 20-LITER BATCHES OF 9% H SOLVENT

| BATCH NO. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Specific Gravity, 60/60°F | 1.026 | 1.024 | 1.025 | 1.023 | 1.023 | 1.024 | 1.025 | 1.024 | 1.024 |
| Carbon, Wt. % | 89.59 | 89.95 | 89.54 | 90.02 | 89.33 | 90.70 | 90.36 | 90.46 | 90.68 |
| Hydrogen, Wt. % | 9.12 | 9.25 | 9.27 | 9.13 | 9.06 | 9.24 | 9.14 | 9.18 | 9.07 |
| Nitrogen, Wt. % | 0.11 | 0.10 | 0.11 | 0.09 | 0.09 | 0.09 | 0.11 | 0.10 | 0.10 |
| Sulphur, Wt. % | 0.006 | 0.002 | 0.003 | 0.001 | 0.001 | 0.002 | 0.009 | 0.005 | 0.001 |
| Proton Distribution, % | | | | | | | | | |
| $H_{ar}$ (9 - 6 ppm) | 26.76 | | | | 24.62 | | | | 25.78 |
| $H_{\alpha}$ (3.5 - 2 ppm) | 24.75 | | | | 22.39 | | | | 26.56 |
| $H_{\beta}$ (2 - 1.1 ppm) | 35.45 | | | | 40.30 | | | | 37.50 |
| $H_{\gamma}$ (1.1 - 0.4 ppm) | 13.04 | | | | 12.69 | | | | 10.16 |
| Distillation Data, °C (ASTM D-86) | | | | | | | | | |
| IBP | 190 | 173 | 170 | 161 | 161 | 168 | 172 | 168 | 178 |
| 5% | 241 | 243 | 240 | 238 | 240 | 242 | 250 | 250 | 250 |
| 10% | 257 | 256 | 259 | 258 | 262 | 267 | 267 | 268 | 266 |
| 20% | 274 | 272 | 277 | 278 | 280 | 281 | 281 | 280 | 280 |
| 30% | 288 | 287 | 291 | 292 | 292 | 292 | 292 | 292 | 291 |
| 40% | 299 | 299 | 301 | 301 | 305 | 305 | 303 | 305 | 302 |
| 50% | 310 | 310 | 311 | 313 | 312 | 313 | 313 | 313 | 312 |
| 60% | 320 | 320 | 321 | 322 | 323 | 322 | 322 | 323 | 322 |
| 70% | 331 | 333 | 335 | 336 | 335 | 335 | 336 | 336 | 335 |
| 80% | 350 | 349 | 350 | 350 | 352 | 350 | 350 | 350 | 349 |
| 90% | 377 | 378 | 372 | 372 | 374 | 372 | 372 | 375 | 371 |
| 95% | 405 | 411 | 394 | 391 | 395 | 394 | 390 | 396 | 392 |
| EP | 489 | 492 | 464 | 482 | 486 | 496 | 490 | 496 | >500 |

## TASK 3 - CATALYST SCREENING TESTS

Coal hydroliquefaction processes involve a number of mechanical and chemical steps which collectively alter the complex structure of the coal *molecules*. When coal is heated to liquefaction temperatures, pyrolytic rupture of chemical bonds in the coal results in the formation of low-boiling materials and highly reactive free-radicals of heavy coal fragments. The free-radicals so produced can achieve stabilization by accepting hydrogen, in which case liquid product is formed, or by reacting with similar fragments to form less reactive materials.

The cracking of large molecular fragments of coal to smaller fragments during hydroliquefaction can be promoted by the use of catalysts. In addition to promoting cracking, catalysts also function to stabilize free-radicals. Although molecular hydrogen can act directly to stabilize free-radicals if long residence times or sufficiently high temperatures are employed, its activity can be increased substantially through chemisorption on an appropriate catalyst. Consequently in catalytic liquefaction processes coal hydrogenation proceeds via direct catalytic action and by hydrogen transfer from donor molecules. Thus the use of catalysts offers benefits related to enhanced liquid yields and/or lower severity operating conditions.

The objective of Task 3 was to screen a series of potential hydroliquefaction catalysts using a batch autoclave system. Twenty-five

hydrogenation experiments were carried out with Lingan mine coal to evaluate the catalytic behavior of the following materials:

1) $Fe_2O_3$
2) $FeS_2$
3) $FeSO_4$
4) $SnO_2$
5) SnS
6) $SnCl_2$
7) $NiCl_2$
8) $CrCl_2$
9) Ammonium Molybdate
10) NALCOMO 479
11) HDS-1442
12) NALCO NM 502

Each of these materials were thoroughly mixed with the feed coal prior to being tested. The mixtures were prepared in the form of dry pulverized solids. Five runs were made with a combination of two or more of the catalysts. Details related to the levels of metal concentration and the catalyst combinations used are given in Tables 8 and 9.

## 3.1 Procedures

A schematic diagram of the high pressure batch system is shown in Figure 5. The reaction vessel is an Autoclave Engineers 300 $cm^3$ magnedrive packless autoclave. The maximum allowable working pressure of the vessel is 35.16 MPa at 450°C. An internal cooling coil permits rapid cooling of the reaction products.

Each experiment was initiated by charging solid reactants and hydrogenated anthracene oil to the autoclave. A vehicle-to-coal ratio of 2.3:1 was used. The vessel was then sealed, evacuated and

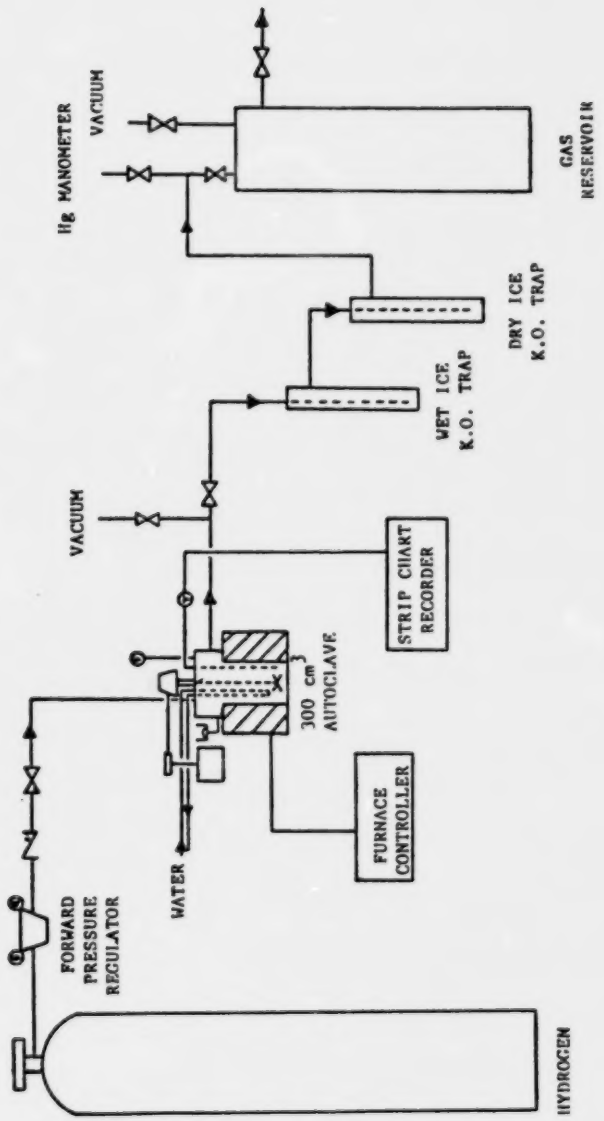



Figure 5 - SCHEMATIC DIAGRAM OF HIGH PRESSURE AUTOCLAVE SYSTEM

charged with hydrogen at room temperature to give the desired pressure at 450°C. The total heat-up time required was about 40-45 minutes, however, only about 6 minutes were required within the zone above 370°C. The reaction was carried out for 30 minutes at 450°C with the stirrer set at 600 rpm. Hydrogen was added to the autoclave during the reaction period to maintain operating pressure if necessary. Pressure was monitored throughout the test period with a dial gauge. Temperature was measured using a chromel-alumel thermocouple and a Philips recorder.

At the end of the reaction period the contents of the autoclave were cooled rapidly to about 130°C. The vessel was depressurized by venting the gases and vapours through wet and dry ice traps into an evacuated 11-liter stainless steel reservoir. At this stage the reaction vessel was cooled to room temperature, isolated from the system and opened.

In this series of tests the reaction products were recovered and extracted with benzene only. The duration of soxhlet extractions was 24 hours. Following this period the extraction thimble and its contents were dried in a vacuum oven at 80°C. After weighing, the dried solids were ashed at 750°C. Conversion, as the proportion of maf coal converted to benzene solubles plus gases, was calculated from an ash balance.

The benzene solubles, oil and asphaltenes, were recovered from benzene using a rotary flash evaporator. Asphaltenes were subsequently precipitated from a portion of the benzene solubles using a large excess

of pentane. The precipitated asphaltenes were then recovered by filtration and extracted in a soxhlet apparatus with pentane. After this step the extraction thimble and its contents were dried to constant weight and the net weight taken as asphaltenes. Oil product was calculated by taking the difference between benzene solubles derived from the feed coal and asphaltenes.

### 3.2 Results and Discussion

Table 8 presents results for Lingan coal in both thermal and catalytic hydrogenation modes. Run Nos.701, 702 and 703were conducted in the thermal mode at 20.68 MPa. Solvents produced from anthracene oil with hydrogen contents ranging from 6.4 to 9.1% were used. As expected, solvent containing 9.1% hydrogen produced the highest conversion to benzene solubles plus gases, 71%, and the highest oil yield, 28%. However, the 7.6% H solvent was used for the catalyst screening tests based on considerations relating to solvent recycle operations in a typical direct catalytic process. Run Nos. 704, 705 and 706 were carried out with commercial hydrotreating catalysts at 20.68 MPa. The Co/Mo and Ni/Mo extruded catalysts were ground to -200 mesh and added at a 5 wt. % level based on dry coal. Results of these tests were quite similar, maf conversion increased to 83% while oil yield rose to the range of 34 - 37%.

In Run Nos. 707 and 708 the catalyst, HDS-1442, was added in extrudate form at levels of 5 and 20 wt. % respectively. Conversion at 20 wt. % catalyst was 83%. Although this conversion was similar to that

TABLE 8

BATCH AUTOCLAVE RESULTS FOR LINGAN COAL IN THERMAL AND CATALYTIC MODES OF OPERATION

| RUN NO. | SOLVENT HYDROGEN CONTENT (WT. %) | OPERATING PRESSURE (MPa) | COAL[1] CHARGED (g) | CATALYST TYPE | CATALYST WT. % | PRODUCTS, WT. % OF maf COAL BENZENE SOLUBLES PLUS GASES | OIL | ASPHALTENES |
|---|---|---|---|---|---|---|---|---|
| 701 | 6.4 | 20.68 | 32.2 | None | | 66 | 24 | 32 |
| 702 | 7.6 | 20.68 | 32.0 | None | | 69 | 25 | 31 |
| 703 | 9.1 | 20.68 | 32.1 | None | | 71 | 28 | 31 |
| 704 | 7.6 | 20.68 | 32.2 | Nalcomo 479** | 5 | 83 | 37 | 37 |
| 705 | 7.6 | 20.68 | 32.0 | Nalco NM 502** | 5 | 83 | 37 | 37 |
| 706 | 7.6 | 20.68 | 31.9 | HDS - 1442** | 5 | 82 | 34 | 38 |
| 707 | 7.6 | 20.68 | 32.2 | HDS - 1442* | 5 | 72 | 23 | 37 |
| 708 | 7.6 | 20.68 | 32.0 | HDS - 1442* | 20 | 83 | 41 | 33 |
| 709 | 6.4 | 13.79 | 32.0 | HDS - 1442** | 5 | 72 | 23 | 39 |
| 710 | 7.6 | 13.79 | 32.1 | HDS - 1442** | 5 | 73 | 25 | 37 |
| 711 | 9.1 | 13.79 | 32.2 | None | | 68 | 25 | 31 |

[1] Lingan (Batch E).
Size and Form of Catalyst: * 1.6 mm extrudate. ** -200 mesh fines.
Reaction Temperature: 450°C. Solvent/Coal Ratio - 2.3:1.
Tests were conducted in a 300 $cm^3$ batch autoclave system.

achieved using -200 mesh HDS-1442 at the 5 wt.% level, oil yield was significantly higher, 41%.

Three experiments were carried out at lower pressure, 13.79 MPa. Two of the tests were catalytic, Run Nos. 709 and 710, using 6.4 and 7.6% H solvents and one was thermal, Run No. 711, with 9.1% H solvent. The results of these tests indicate that catalyst and hydrogen pressures in excess of 13.79 MPa are required to achieve high yields of product oil.

Conversion data in Table 9 illustrate that iron-based compounds such as $Fe_2O_3$, $FeS_2$ and $FeSO_4$ are considerably less active for catalytic coal hydrogenation than $SnCl_2$, $NiCl_2$ and ammonium molybdate. $SnCl_2$ was found to be a superior catalyst for the conversion of coal to oil. Using $SnCl_2$ at a metal concentration of 0.5 wt. % based on dry coal, maf conversion and oil yield were 85 and 41% respectively. Oil yields were enhanced further using $SnCl_2$ in combination with Ni/Mo and Co/Mo. The highest oil yield, 49%, was produced in Run No. 723 with $NiCl_2$, $SnCl_2$ and ammonium molybdate as catalyst. Run No. 725 was made to evaluate the effect of $SnCl_2$ in combination with HDS-1442. Conversion and oil yield were 87 and 46% respectively. Figure 6 shows the effects of $SnCl_2$ and HDS-1442, separately and together, on maf conversion and oil yield.

Simulated distillations of benzene solubles from selected experiments are given in Table 10. The data indicates that the coal-derived liquids have both lighter and heavier boiling fractions than the starting solvent, HAO 2. However, it is not possible to rank the

TABLE 9

RESULTS OF BATCH AUTOCLAVE CATALYST SCREENING TESTS

| RUN NO. | CATALYST | METAL CONCENTRATION[1] (Wt. %) | COAL CHARGED (g) | PRODUCTS, WT. % OF maf COAL | | |
|---|---|---|---|---|---|---|
| | | | | BENZENE SOLUBLES PLUS GASES | OIL | ASPHALTENES |
| 702 | None | - - | 32.0 | 69 | 25 | 31 |
| 712 | $Fe_2O_3$ | 3.50 | 32.1 | 67 | 25 | 35 |
| 713 | $FeS_2$ | 2.33 | 32.2 | 72 | 21 | 37 |
| 714 | $FeSO_4$ | 1.84 | 31.9 | 74 | 30 | 33 |
| 715 | $SnO_2$ | 3.94 | 32.1 | 79 | 31 | 38 |
| 716 | SnS | 3.94 | 32.0 | 67 | 25 | 33 |
| 717 | $SnCl_2$ | 0.50 | 32.1 | 85 | 41 | 35 |
| 718 | $NiCl_2$ | 0.50 | 32.1 | 81 | 35 | 33 |
| 719 | $(NH_4)_6Mo_7O_{24}.4H_2O$ | 0.50 | 32.0 | 80 | 32 | 39 |
| 720 | $(NH_4)_6Mo_7O_{24}.4H_2O/NiCl_2$ | 0.50/0.50 | 32.0 | 87 | 39 | 34 |
| 721 | $(NH_4)_6 Mo_7O_{24}.4H_2O/NiCl_2/SnCl_2$ | 0.50/0.50/0.50 | 32.1 | 86 | 46 | 29 |
| 722 | $(NH_4)_6Mo_7O_{24}.4H_2O/NiCl_2/SnCl2$ | 0.25/0.25/0.25 | 32.0 | 86 | 41 | 36 |
| 723 | $(NH_4)_6Mo_7O_{24}.4H_2O/NiCl_2/SnCl_2$ | 0.75/0.75/0.75 | 31.9 | 88 | 49 | 27 |
| 724 | $CrCl_2$ | 0.25 | 32.0 | 84 | 40 | 35 |
| 706 | HDS-1442 (Co/Mo) | 0.12/0.48 | 31.9 | 82 | 34 | 38 |
| 725 | HDS-1442/$SnCl_2$ | 0.12/0.48/0.50 | 32.1 | 87 | 46 | 32 |

[1] Metal concentration on dry coal basis. Lingan Coal (Batch E) used for all tests.
Reaction Conditions: Temperature 450°C; Pressure 20.68 MPa; Time 30 minutes; Solvent Hydrogen Content 7.6%; Solvent/Coal Ratio 2.3:1
Experiments conducted in a 300 $cm^3$ autoclave system.

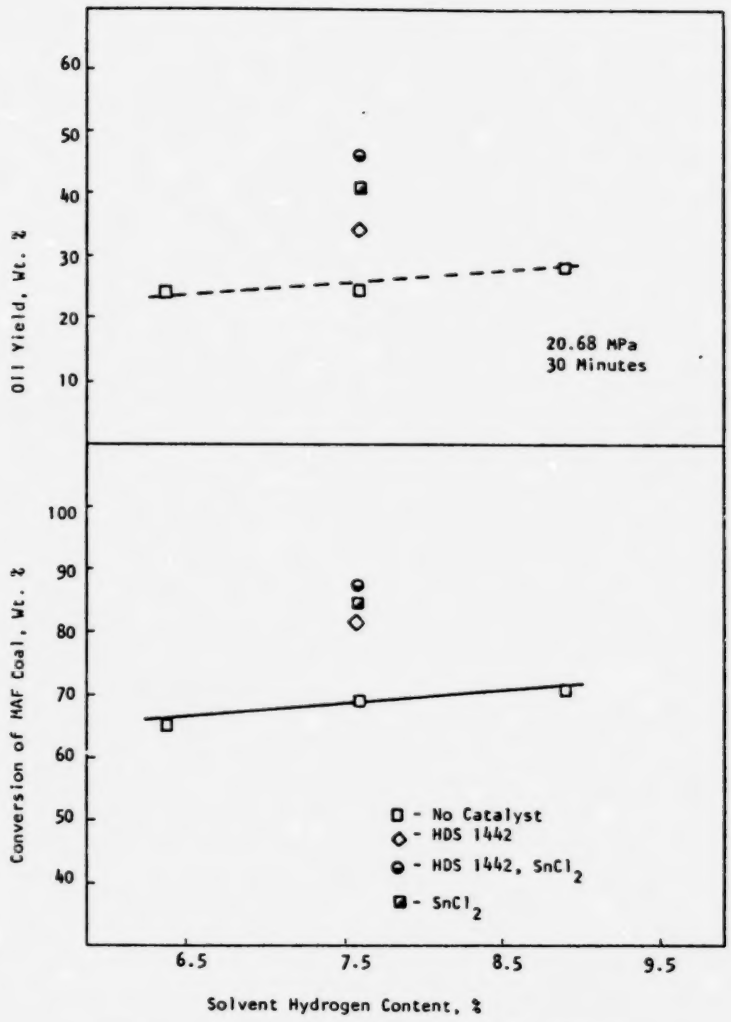



Figure 6 - INFLUENCE OF CATALYSTS ON CONVERSION OF LINGAN COAL AT 450°C

TABLE 10

SIMULATED DISTILLATION OF BENZENE-SOLUBLE FRACTIONS
FROM CATALYST SCREENING TESTS

| | HAO 2 | RUN NO. 702 | RUN NO. 704 | RUN NO. 705 | RUN NO. 706 |
|---|---|---|---|---|---|
| DISTILLATION DATA, °C (Simulated by Gas Chromatography) | | | | | |
| IBP/5 | 195/220 | 179/211 | 182/210 | 183/212 | 182/211 |
| 10/30 | 247/292 | 238/288 | 238/288 | 239/288 | 239/288 |
| 50 | 319 | 319 | 318 | 318 | 318 |
| 70/90 | 350/389 | 358/398 | 349/396 | 351/397 | 351/395 |
| 95/EP | 412/469 | 432/492 | 430/497 | 429/488 | 426/490 |

| | RUN NO. 708 | RUN NO. 717 | RUN NO. 718 | RUN NO. 723 | RUN NO. 725 |
|---|---|---|---|---|---|
| DISTILLATION DATA, °C (Simulated by Gas Chromatography) | | | | | |
| IBP/5 | 179/210 | 183/211 | 177/210 | 176/209 | 179/210 |
| 10/30 | 237/287 | 239/288 | 237/288 | 234/287 | 237/287 |
| 50 | 318 | 318 | 319 | 318 | 319 |
| 70/90 | 351/397 | 354/397 | 358/399 | 356/400 | 356/399 |
| 95/EP | 433/490 | 431/502 | 433/487 | 438/495 | 435/494 |

catalysts in terms of hydrocracking efficiency from this data due to the variable degree of coal solvation and the dilution effect caused by the presence of vehicle oil.

Elemental analysis on pentane solubles and benzene solubles from the catalyst screening tests are shown in Table 11. It should be noted that the three commercial hydrotreating catalysts exhibited similar hydrogenation and denitrogenation activities. However, Nalcomo 479 and NALCO NM502 showed slightly higher desulphurization activity than HDS-1442. This is most likely attributable to the higher concentration of metals in the NALCO preparations. As expected the Ni/Mo, Ni/Mo/Sn and Co/Mo/Sn functioned effectively as desulphurization catalysts. $Fe_2O_3$ was also influencial in reducing the sulphur content of the coal liquid. In regard to nitrogen removal Ni, Mo and Sn appear to be the most active combination tested.

During the catalyst screening experiments it was observed that the autoclave wall became catalytically activated from stannous chloride. This *memory effect* influenced conversion and oil formation in a positive manner. Two procedures were found to be effective in eliminating the influence of this factor on subsequent experiments. Firstly, tests with stannous chloride were carried out using a glass liner in the reactor. Secondly, blank runs were carried out with hydrogenated anthracene oil (7.5% H) and molecular hydrogen at 450°C for two hours following an experiment in which stannous chloride was used. It was postulated that formation of chromium chloride on the wall of the reactor may con-

TABLE 11

ELEMENTAL ANALYSIS ON PENTANE AND BENZENE SOLUBLES FROM CATALYST SCREENING TESTS

| RUN NO. | PENTANE SOLUBLES | | | | BENZENE SOLUBLES | | | |
|---|---|---|---|---|---|---|---|---|
| | C (Wt.%) | H (Wt.%) | N (Wt.%) | S (Wt.%) | C (Wt.%) | H (Wt.%) | N (Wt.%) | S (Wt.%) |
| 701 | 90.82 | 6.40 | 0.64 | 0.192 | 91.52 | 6.54 | 0.80 | 0.200 |
| 702 | 91.05 | 7.15 | 0.42 | 0.058 | 91.53 | 7.01 | 0.61 | 0.083 |
| 703 | 90.93 | 8.30 | 0.23 | 0.026 | 90.59 | 8.10 | 0.43 | 0.055 |
| 704 | 91.04 | 7.78 | 0.46 | 0.047 | 90.63 | 7.52 | 0.67 | 0.056 |
| 705 | 90.87 | 7.79 | 0.46 | 0.045 | 90.23 | 7.53 | 0.65 | 0.054 |
| 706 | 90.64 | 7.61 | 0.45 | 0.062 | 90.05 | 7.40 | 0.65 | 0.079 |
| 707 | 91.19 | 7.25 | 0.41 | 0.060 | 90.55 | 7.17 | 0.60 | 0.083 |
| 708 | 91.55 | 8.00 | 0.46 | 0.044 | 89.68 | 7.49 | 0.61 | 0.054 |
| 709 | 91.52 | 6.72 | 0.58 | 0.181 | 91.11 | 6.57 | 0.80 | 0.188 |
| 710 | 91.80 | 7.40 | 0.38 | 0.067 | 91.12 | 7.25 | 0.64 | 0.079 |
| 711 | 90.19 | 8.04 | 0.21 | 0.026 | 90.92 | 7.92 | 0.42 | 0.052 |

TABLE 11 (Continued)

ELEMENTAL ANALYSIS ON PENTANE AND BENZENE SOLUBLES FROM CATALYST SCREENING TESTS

| RUN NO. | PENTANE SOLUBLES | | | | BENZENE SOLUBLES | | | |
|---|---|---|---|---|---|---|---|---|
| | C (Wt.%) | H (Wt.%) | N (Wt.%) | S (Wt.%) | C (Wt.%) | H (Wt.%) | N (Wt.%) | S (Wt.%) |
| 702 | 91.05 | 7.15 | 0.42 | 0.058 | 91.53 | 7.01 | 0.61 | 0.083 |
| 712 | 90.94 | 7.37 | 0.43 | 0.051 | 90.74 | 7.22 | 0.62 | 0.067 |
| 713 | 90.76 | 7.27 | 0.43 | 0.061 | 90.18 | 7.02 | 0.64 | 0.079 |
| 714 | 89.74 | 7.87 | 0.47 | 0.058 | 90.72 | 7.32 | 0.62 | 0.073 |
| 715 | 90.55 | 7.64 | 0.42 | 0.052 | 90.31 | 7.32 | 0.65 | 0.067 |
| 716 | 90.00 | 7.71 | 0.45 | 0.055 | 89.75 | 7.47 | 0.61 | 0.074 |
| 717 | 89.64 | 7.61 | 0.43 | 0.053 | 89.54 | 7.51 | 0.61 | 0.072 |
| 718 | 90.07 | 7.62 | 0.45 | 0.052 | 89.66 | 7.47 | 0.62 | 0.071 |
| 719 | 90.29 | 7.50 | 0.44 | 0.061 | 90.55 | 7.02 | 0.66 | 0.079 |
| 720 | 89.99 | 7.74 | 0.45 | 0.049 | 90.18 | 7.63 | 0.61 | 0.062 |
| 721 | 90.47 | 7.61 | 0.43 | 0.062 | 89.67 | 7.36 | 0.58 | 0.064 |
| 722 | 90.96 | 7.79 | 0.43 | 0.060 | 90.68 | 7.48 | 0.61 | 0.069 |
| 723 | 90.87 | 7.79 | 0.42 | 0.051 | 91.25 | 7.42 | 0.54 | 0.059 |
| 724 | 90.95 | 7.70 | 0.47 | 0.058 | 90.36 | 7.46 | 0.62 | 0.065 |
| 706 | 90.64 | 7.61 | 0.45 | 0.062 | 90.05 | 7.40 | 0.65 | 0.079 |
| 725 | 91.21 | 7.58 | 0.46 | 0.052 | 89.45 | 7.26 | 0.60 | 0.058 |

tribute to the *memory effect*. Hence Run No. 724 was conducted to investigate the catalytic behavior of chromium chloride. Significant increases in conversion, 69 to 84%, and oil formation, 25 to 40%, were observed.

# TASK 4 - LITERATURE REVIEW: SEPARATION AND CHARACTERIZATION OF COAL LIQUIDS

## 4.1 Introduction

Direct coal conversion processes fall into three broad categories - pyrolysis, solvent extraction and catalytic hydrogenation. Each of these processing schemes results in the production of coal liquids which contain a variety of desirable and undesirable components. The raw liquids are relatively unstable during storage and a more complete knowledge of their composition is required than has been necessary for petroleum. Detailed characterization of coal liquids is prerequisite to their upgrading and utilization.

Since coal liquefaction products are extremely complex mixtures, it is advantageous to apply separation steps prior to detailed characterization. Analytical separation techniques normally used for petroleum crudes or residues have been successfully applied to coal liquefaction products. This literature review covers a wide range of analytical methods that have been used to separate and characterize coal-derived liquids.

## 4.2 SEPARATION METHODS

### 4.2.1 Solvent Extraction

This procedure is commonly used for isolating the liquid products of coal conversion. Generally solvent analysis schemes are based on the solubility of coal-derived products in pentane, benzene and pyridine. Oils are operationally defined as pentane solubles, asphaltenes as the benzene-soluble and pentane-insoluble fraction and preasphaltenes as the pyridine-soluble and benzene-insoluble fraction. In some procedures toluene is substituted for benzene and tetrahydrofuran (THF) is substituted for pyridine. Samples are usually Soxhlet extracted, however, a variety of extraction sequences have been used.

The effect of the extraction sequence on product distributions has been reported by Ruberto and Cronauer (5). They examined three extraction sequences; direct, forward sequential and reverse sequential. Both sequential approaches gave results that were not as meaningful as those from the direct approach. In fact, both of the sequential methods suffer as a result of drying the samples between the extraction steps. Actually, drying appears to promote *repolymerization.* They suggested that standard analytical methods be adopted for the determination of these products.

Mima et al. (6) reported on the procedure used at the Pittsburg Energy Research Center for the determination of oils and asphaltenes in coal-derived liquids. The procedure involved an extraction with benzene followed by precipitation of the asphaltenes using a large excess of pentane. The precipitation of asphaltenes from coal-

derived liquids was also investigated by Bockrath et al. (7). They used toluene and pentane to separate oil and asphaltenes from Synthoil products. This investigation showed that the precipitation of asphaltenes must be rigorously controlled. The precipitation was carried out by adding a large excess of pentane to a slurry prepared from the toluene solubles and toluene. A significant difference was found in the values determined for asphaltenes depending upon the amount of toluene used in the slurry.

Bockrath et al. (8) also separated coal-derived asphaltenes into acid-neutral and base components by passing dry HCl through their benzene solution according to the method of Sternberg et al. (9). Taylor et al. (10) also used the method of Sternberg for acid/base fractionation of asphaltenes. These fractions were used to investigate the nature of hydrogen bonding in coal-derived liquids. This was achieved by using proton NMR spectroscopy.

Schweighardt and Thames (11) added a pre-treatment step to solvent analysis. Liquid nitrogen was used to freeze the sample. The sample was then ground to a powder and extracted with pentane. The increased surface area increased the efficiency of the extraction. The pentane insolubles were extracted with THF.

Schwager and co-workers (12) separated coal-derived liquids from five major processes using pentane, benzene, propane and carbon disulphide. Samples were separated into solubles and insolubles using a 20-fold excess of pentane. The pentane solubles were further separated into resins and oil using liquefied propane. The pentane in-

solubles were treated with benzene to extract asphaltenes. Finally, the benzene insolubles were treated with carbon disulphide to yield carbene and carboid species.

### 4.2.2. Distillation

Laboratory-scale distillation has been applied to heavy petroleum crude oils to obtain distillate fractions for comprehensive analytical characterization. Colemen et al (13) used a molecular still operating at high temperatures and reduced pressures to prepare broad-boiling-range distillates (e.g.; 225-315°C, 315-370°C, 370-535 and 535-675°C). This continuous-flow apparatus provides a short residence time for the sample in the heated zone. The still uses wiper blades mounted on a rotor in the interior to spread the sample in a thin film over the heated wall where distillation is effected. To prepare more precise fractions in the mid-distillate boiling range, distillation equipment such as a spinning band column may be used.

### 4.2.3. Liquid Chromatography

Liquid column chromatography is a physical separation process involving a stationary solid phase through which a mobile liquid phase flows. In adsorption chromatography the separation is based on repeated adsorption-desorption steps whereas in ion-exchange chromatography the stationary bed has an ionically charged surface of opposite charge to the sample. Chromatographic procedures have been used to separate petroleum distillates into hydro-

carbon groups and chemical classes. Small columns yield only limited quantities of material for analysis. However, preparative-scale chromatographic columns have been used to obtain larger amounts of materials.

Lumpkin and Aczel (14) used a modified version of the clay-gel adsorption chromatographic method, ASTM D-2007, to separate fractions boiling above the naphtha range into saturate, aromatic and polar fractions. White et al. (15) used fluorescent indicator adsorption (FIA) chromatography, ASTM D-1319, to separate light oil from coal liquids. The FIA method covers the determination of saturates, non-aromatic olefins and aromatics in petroleum fractions that distill below 315°C. The light oil fractions were analyzed by GC-MS, infrared and Raman spectroscopy.

A method for the separation of high-boiling petroleum distillation into saturates, monoaromatics, diaromatics and polyaromatic-polar concentrates was developed by Hirsch et al. (16). The procedure utilizes both silica and alumina gels in a single column. Separation is achieved by sequential elution with various solvents. Approximately 10 liters of mobile phase is required per sample passed through the column. This method has been applied to coal syncrude distillates. Inoue et al. (17) used a silica-alumina dual-packed column to separate the oil products from batch autoclave tests into saturates, monoaromatics, diaromatics, tri- and tetra-aromatics, polyaromatics and polar compounds and basic nitrogen compounds. The chemical compositions of

these compound types were investigated by means of elemental analysis, molecular weight measurements and proton NMR spectroscopy. Proton assignments were based on the method of Brown and Ladner (18).

Schiller and Mathiason (19) fractionated coal derived solids and heavy liquids on neutral alumina for subsequent analysis by mass spectrometry and other spectral methods. The principal compound types eluted were; saturated hydrocarbons, aromatic hydrocarbons and benzofurans, ethers, nitrogen compounds and hydroxyl compounds.

Several investigators have reported on separation schemes using silica-gel chromatography. Schweighardt et al. (20) isolated four major molecular types, including a heteroatom fraction containing oxygen and nitrogen, from Synthoil product using hexane, benzene and tetrahydrofuran. The chromatographic fractions were examined by $^{1}H$ and $^{13}C$ high field NMR spectroscopy. Schabron et al. (21) used a silica gel open-column to separate alkylphenols from coal liquefaction recycle solvent samples. Fractions rich in mono-ortho and non-ortho substituted alkylphenols were isolated. The fractions were separated further by high-performance liquid chromatography (HPLC) and characterized by base extraction, chemical spot tests and ultraviolet adsorption and fluorescence spectroscopy in neutral and basic solutions. Coal-derived asphaltenes from five major demonstration processes in the United States were separated on a silica gel preparative-scale column using benzene, diethyl ether and THF by Schwager and Yen (22). Chemical and instrumental methods were used to deduce features of the microstructures of these asphaltenes.

A combination of ion exchange, coordination and adsorption chromatography was employed by Jewell et al. (23, 24) for the separation of heavy-end petroleum distillates. This method has also been used to separate coal-derived products into five fractions: acids, bases, neutral nitrogen compounds, saturated hydrocarbons and aromatic hydrocarbons. This method is commonly known as the SARA technique (saturates, aromatics, resins and asphaltenes) and has been widely used. Later and co-workers (25) developed a chemical class separation using neutral alumina and silicic acid adsorption chromatography. The principal chemical classes investigated in a solvent refined coal liquid were aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polycyclic aromatic sulphur heterocycles, nitrogen polycyclic aromatic compounds and hydroxyl polycyclic aromatic hydrocarbons. Jones et al. (26) used Sephadex LH-20 gel for the class fractionation of syncrudes to provide samples for biological testing. A coal-derived and a shale-derived oil were separated into aliphatic hydrocarbons, one- and two-ring aromatics and polynuclear aromatics.

### 4.2.4 High Pressure Liquid Chromatography

Procedures for routine liquid chromatographic separations of hydrocarbon classes in petroleum and coal liquid samples have been improved by use of high performance liquid chromatography (HPLC) techniques. HPLC provides rapid, reproducible analysis of complex mixtures. Separation techniques are normally developed on analytical columns to conserve solvent, time and sample material. Once the analytical separation has been developed, scale-up to preparative fractionation can be undertaken to isolate sufficient material for subsequent characterization.

Vogh and Thomson (27) used alumina and silica gel to fractionate a Utah coal syncrude, B.P. range 200-370°C, into saturates, monoaromatics, diaromatics, polyaromatic-polars, acids and bases. Their results were in good agreement with data obtained using the API-60 Method (16). One obvious advantage of this method is the saving of time. The complete operation takes about 2 hours compared with 50 hours continuous run time with the API-60 open-column method. According to the author the columns are reusable and offer reliably good resolution and repeatability.

Miller et al. (28) separated a coal liquefaction process stream into paraffins, olefins, aromatics and resins using an amino-cyano analytical column (Perkin-Elmer Corporation). The procedure involves forward elution with pentane and a backflush operation with methyl-t-butyl ether. Differential refractometry and ultraviolet (UV) detection were used to monitor the column effluent. Dark and McFadden (29) obtained saturate, aromatic and polar fractions from an asphaltene free coal liquid sample on a μBONDPAK $NH_2$ column (Waters Associates). n-Heptane was used as the mobile phase.

Dark et al. (30) also reported an HPLC separation technique based on the number of condensed rings. Fractionation was demonstrated on both analytical and preparative-scale columns packed with μPORASIL (silica gel). In the preparative mode, 500 milligrams of oil was separated in 16 minutes. Katoh et al. (31) used μBONDAPAK $NH_2$ to separate a coal liquid into fractions having a different number of aromatic rings. Each fraction was further separated into secondary fractions based on the number of carbon atoms using reversed phase HPLC.

The chromatographic behavior of a number of typical hydrocarbons, fully aromatic and partially hydrogenated, was described by Liphard (32). A coal oil fraction, B.P. range 210-270°C, was separated on LiChrosorb $NH_2$ (Hewlett Packard) with n-hexane as the mobile phase. The separation is controlled by the number of double bonds present in a given hydrocarbon molecule. In the case of the middle oil considered here the analysis can be carried out in 8 minutes.

Prather et al. (33) used HPLC to study the hydrogenation/desulphurization of creosote oil. This coal-derived oil has been used as a start-up solvent in coal liquefaction processes. Two 4 mm (ID) x 30 cm microbondapak/$C_{18}$ columns (Waters Associates) were used in series to separate the creosote components. The major components identified fall into two categories: polynuclear aromatics and heteroatom compounds.

Analysis of coal conversion recycle solvents via HPLC with a continuous-flow H-NMR detector was reported by Haw et al. (34). The on-line LC/H-NMR analysis was complemented with a GC-MS analysis of off-line LC-fractions. A Whatman Magnum-9 silica gel-PAC column was used for normal-phase separations. The LC/H-NMR technique characterized the hydrocarbons and aromatic ethers with a level of certainty not achievable with conventional detectors.

A technique for separating and identifying phenols in coal liquids, petroleum and shale oils was described by King-Jou Chao and Suatoni (35). Thirty-eight phenol model compounds were separated and response factors established.

Chmielowiec and George (36) reported on the application of polar bonded-phase sorbents to the HPLC separation of polycyclic aromatic hydrocarbons. They found a silica-based diamine sorbent to be superior to six other silica-based column materials studied.

Holstein and Severin (37) studied 15 commercially available stationary phases. Their objective was to get well resolved chromatograms as fingerprints of various fractions from coal-derived oil. Group-type separation yielded the following fractions: acids, bases, nonbasic heterocompounds, saturates, monoaromatics, diaromatics and polyaromatics. Each fraction was chromatographed on all of the stationary phases. According to the authors unmodified silica and alumina supports can be used for group-type separation schemes but they are not suitable for separations which require high resolution. They found tetranitrofluorenonsilica (TNF) to be useful for characterizing coal liquids by their fingerprint chromatograms.

### 4.2.5 Gel-Permeation Chromatography

Gel-permeation chromatography (GPC) is a technique in which fractionation is based, at least in part, upon the molecular size and shape of the species in the sample. This technique has several names; e.g., gel chromatography, exclusion chromatography and molecular-sieve chromatography. Ordinarily, gel chromatography is carried out on a column by the elution method. The column packing has precisely controlled pore sizes and molecules or ions larger than the pores of the gel are completely excluded from the interior while smaller species are more or less free to enter these regions. Therefore, larger

molecules pass quickly through the column while smaller ones are retarded to a greater or lesser degree depending upon their size, shape and sometimes upon their tendency to be adsorbed by the stationary phase.

Yokoyama et al. (38, 39) separated the hexane-soluble oil fraction from hydrogenated coal into saturate and aromatic fractions by liquid chromatography using a silica gel column. They went on to separate saturate oil, aromatic oil as well as asphaltenes by GPC. Their GPC results, using crosslinked polystyrene gels, were in agreement with molecular weight measurements for the fractions determined by vapor pressure osmometry (VPO).

Coleman et al. (40) investigated size separation of the THF-soluble fraction of solvent refined coal (SRC) using numerous molecular-size separators. The following materials were studied: μ Styragel, Styragel (60 Å), Licrosphere (100 Å), Bio-Beads S-X12 and Bio-Beads S-X4. They reported an effective separation into four fractions using Bio-Beads S-X4. These investigators also demonstrated preparative-scale quantitative separation of THF- and $CHCl_3$-soluble SRC employing gel permeation chromatographic techniques (41). Average molecular weights via VPO on the four sized fractions of THF-soluble SRC from Bio Beads suggest that a separation according to molecular weight was achieved. Hathaway et al. (42) used GPC and HPLC in combination with infrared spectrometry, UV absorption, fluorscence and mass spectrometry to characterize four SRCs. GPC was performed using three μ-styragel columns; sizes 500 Å, 100 Å and 100 Å, in series with THF as mobile phase.

Philip and Anthony (43 - 45) described three separate GPC systems for the fractionation of coal-derived liquids. They arranged as many as four 100 Å μ Styragel columns in series. THF and toluene were used as mobile phases. Characterization of volatile components in various GPC fractions was accomplished by gas chromatography and high resolution GC-MS.

Mayo and Kirshen (46) developed a calibration curve for the determination of molecular weight by GPC using fractions of extracts and SRCs of Illinois and Kentucky coals. They found that for most of the pyridine, toluene and hexane-soluble fractions, the GPC peaks are fairly sharp but VPO gives a more precise and convenient measure of molecular weights than GPC. However, further fractionation by other solvents or chemical reaction may require molecular weight determination by GPC.

### 4.2.6. Gas-Liquid Chromatography

In gas chromatography the components of a vaporized sample are separated as a result of partition between a mobile gaseous phase and a stationary phase retained in a column. In gas-liquid chromatography (GLC) the stationary phase is a liquid normally supported on an inert solid matrix. The rate of movement of the various sample components along the column is dependent upon their tendency to dissolve in the stationary phase. Separation by this method of chromatography is only possible for volatile components.

Lee and co-workers (47) developed a retention index for polycyclic aromatic hydrocarbons (PAH) using programmed-temperature capillary-column gas chromatography. The columns were made by coating glass capillary tubing with SE-52 methylphenylsilicone as stationary phase. Retention indices were calculated for over 200 PAH standard compounds. The retention index was defined based on the series of PAH internal standards: naphthalene, phenanthrene, chrysene and picene. According to the authors, this system offers significant advantages in attempts to identify isomeric PAH in complex mixtures. Stompel et al (48) used the procedure of Lee to identify more than 150 compounds in tars produced from the pyrolysis of coal.

Kong et al (49) used capillary column gas chromatography to resolve isomeric polycyclic aromatic sulphur heterocycles in a coal liquid. Fused silica capillary columns coated with nonpolar, polar and liquid crystal stationary phases and their mixtures were evaluated. All of the 3-, 4- and 5-ring polycyclic aromatic sulphur heterocycles were resolved and identified.

Simulated or chromatographic distillation (ASTM D-2887) has been widely used for obtaining boiling point data of petroleum-based materials. Pannell and Sood (50) recently compared simulated distillation of oil fractions produced by coal liquefaction to true-boiling-point (TBP) distillations. They found that the simulated distillation and TBP data agree well. Furthermore, they reported that the repeatability of the chromatographic distillation was excellent.

## 4.3 CHARACTERIZATION METHODS

### 4.3.1 Fluorescence and Ultraviolet Spectroscopy

Fluorescence spectroscopic analysis has been used to detect polynuclear aromatic hydrocarbons in coal tar and high boiling petroleum fractions (51, 52). The successful application of fluorescence to the analysis of coal-derived liquids depends on good separation of the hydrocarbon mixture. Kershaw (53) demonstrated the potential of this analytical technique for the identification of polyaromatic ring systems in coal hydrogenation liquids and coal extracts. The oils were separated by adsorption chromatography on silica gel. Twelve aromatic ring systems were identified. Katoh et al. (31) used synchronous fluorescence spectrometry to study condensed aromatic ring systems in HPLC fractions.

Searl et al. (54) developed a routine method to measure polynuclear aromatic compounds in coke oven effluents using gas chromatography and ultraviolet absorption spectrometry. UV absorption spectra of selected GC fractions provide a quantitative measurement of fluoranthene, pyrene, benz [a] anthracene, chrysene, benzo [a] pyrene, benzo [e] pyrene, benz [c] acridine and benz [a] anthrone. Hathaway et al. (41) used UV and fluorescence to investigate GPC fractions of SRCs. Recently, Schabron et al. (21) utilized UV and fluorescence to identify phenols in liquid chromatographic fractions of coal liquefaction recycle solvents.

### 4.3.2 Infrared Spectroscopy

Infrared (IR) spectroscopy has been widely utilized to detect and quantify functional groups in coal conversion

products. The advent of computerized Fourier-transform instruments (FTIR) has opened up new possibilities for the infrared spectroscopic characterization of coal and coal liquids. FTIR offers considerable advantages over conventional dispersive methods for the characterization of highly absorbing materials.

Brown et al. (55) characterized coal-derived asphaltenes and their acid and basic components by IR. The assigned peaks to phenolic OH, acid nitrogen NH and hydrogen-bonded acidic components. Bockrath et al. (8, 56) used the IR peak assignments of Brown et al. to characterize pentane- and benzene soluble fractions of coal liquids. The spectra indicated the presence of phenolic OH and acidic nitrogen. Schwager and Yen (57) analyzed Synthoil asphaltene and silica-gel chromatography fractions for hydroxyl oxygen and pyrrolic nitrogen by IR.

Gould et al. (58) used IR in their studies on the viscosity of coal liquefaction bottoms. They found that hydrogen bonding can make a significant contribution to the viscosity of coal-derived products. Taylor (10) reported on the nature of hydrogen bonding in coal-derived asphaltenes using near-infrared and H-NMR techniques. They found that the use of a Co/Mo catalyst leads to a base asphaltene component of lower molecular weight and higher hydrogen-bond acceptor strength. They concluded that more work is necessary before a complete explanation of the relation of product-oil viscosity to hydrogen bonding in coal-derived asphaltenes can be given.

Bodzek et al. (59) studied the basic and acidic/neutral fractions of asphaltenes using IR, thin-layer chromatography, H-NMR and MS. They found that the asphaltenes derived from two liquefaction processes with three bituminous coals were appreciably similar. The analytical data indicated that the asphaltenes were essentially acid-base complexes linked by hydrogen bonds.

Curtis et al. (60) obtained a qualitative indication of the relative amounts of aliphatic and aromatic hydrogen present in numerous coal liquefaction solvents using IR. An infrared absorbance ratio was established by measuring the aromatic C-H stretch at 3050 $cm^{-1}$ and the aliphatic C-H stretch at 2925 $cm^{-1}$. They presented results for the conversion of Wyoming and Kentucky coals as a function of this solvent parameter.

FTIR was used by Painter and Coleman (61) to determine the functional groups present in three SRC samples. Hathaway et al. (62) applied FTIR to fractions isolated by GPC.

### 4.3.3 Nuclear Magnetic Resonance Spectrometry

The potential of nuclear magnetic resonance (NMR) in coal science has long been recognized. NMR techniques offer a means for obtaining both structural and quantitative information. In 1960, Brown and Lander (18), introduced a method based on proton magnetic resonance (H-NMR) to estimate carbon aromaticities for liquid and soluble materials from coal. This method has been further developed by other investigators (63-68).

Schweighardt, Friedel and Retcofsky (69) used multi-nuclei magnetic resonance to study the hydrogen bonding of the acid and base components of coal-derived asphaltenes. Structural aspects of sub-bituminous coal were deduced from solvation studies using H-NMR, MS and GLC by Ruberto et al. (70). Oka, Chang and Gavalas (71) developed a computer-assisted molecular structure construction technique for the structural elucidation of coal-derived compounds. This technique utilizes NMR spectra, elemental analysis and molecular weight data to determine the allowable combinations of functional groups constituting the structure.

The carbon-13 NMR spectra of solid coals have been compared to those of the coal-derived liquids (72). It was noted that certain bands visible in the solid are no longer present in the liquefied state. Yokoyama et al. (73) used H-NMR, carbon-13 NMR, GPC and gas chromatography for the structural characterization of coal hydrogenation products. Seshadri and co-workers (74) discussed the carbon-13 spectra and spectra-structure correlation of model hydroaromatic hydrocarbons, related compounds and fractions from partially hydrogenated condensed aromatic hydrocarbons.

Whitehurst, Farcasiu and Mitchell (75) used H-NMR and gas chromatography to characterize pilot plant recycle streams. GPC fractions of SRC were analyzed quantitatively by Wooton et al (76) using proton and carbon-13 Fourier-transform NMR. According to the authors accurate monitoring of aliphatic and aromatic H/C ratios for each fraction could provide a convenient means of monitoring hydrogen utilization in SRC

processes. Curtis et al. (60) characterized numerous hydrogenated creosote oils and SRC recycle solvents by spectroscopic measurement of their hydrogen distribution. Elevated temperature carbon-13 Fourier-transform NMR has also been used to measure hydrogen to carbon ratios in SRC (77).

An NMR method has been described for the characterization and quantitation of hydroxyl groups in complex organic mixtures by Schweighardt et al. (78). They applied this method to the characterization of hydroxyl groups found in coal liquefaction oils and asphaltenes.

H-NMR, carbon-13 NMR and capillary gas chromatography were utilized by Farnum and Farnum (79) to characterize fractions isolated from lignite-derived light oils. Forty hydrocarbons and six phenolic compounds were identified and quantitatively measured.

### 4.3.4 Mass Spectrometry

Coal-derived liquids may well be the most complex mixtures of organic compounds ever encountered. Due to the complexity of coal syncrudes, primary emphasis is placed on determining the most probable types (families) of compounds present. The electron impact (EI) ionization mode of mass spectrometry (MS) is not totally suitable for the analysis of these liquids because this technique produces excessive fragmentation of the molecules. In recent years field ionization/mass spectrometry (FI/MS) has been applied to the compositional analysis of coal liquids by several investigators (59, 80, 81, 82). In FI/MS the sample need not be vaporized for ioniz-

ation and thus even non-volatile components can be ionized without decomposition. Furthermore, this technique mainly produces molecular ions by suppressing the formation of fragment ions and hence gives a simple mass spectrum.

Lumpkin and Aczel (14) extended MS techniques for petroleum to the characterization of coal liquids. They analyzed the saturate fraction of material boiling above the naphtha range by the high ionizing voltage MS method, ASTM D-2786. The aromatic and polar fractions were determined using a high resolution instrument operated in the low ionizing voltage mode (83).

Dark et al. (30) examined fractionated coal liquids by chemical ionization (CI) mass spectrometry. This technique produces less fragment ions than the EI method. Later et al. (25) operated a quadrapole MS in the EI mode to identify individual components fractionated by capillary column gas chromatography.

Hazlett and co-workers (84) made structural assignments to specific GC/MS peaks through comparison with pure compounds. Low resolution MS was used by Katoh et al. (31) to aid in the characterization of HPLC fractions. Schiller and Mathiason (19) utilized GC-MS and high resolution MS to study fractions obtained from a Co-Steam product and a gasifier tar.

TASK 5 - INSTALLATION AND OPERATION OF NEW EQUIPMENT

The purpose of Task 5 was to modify and upgrade our bench-scale continuous coal liquefaction unit. Activities under this task included the procurement, installation and commissioning of the following equipment:

(1) Continuous stirred tank reactor complete with furnace and temperature controller. A stand-pipe was installed in this 1500 $cm^3$ reactor to provide a liquid phase capacity of 1020 $cm^3$ at NTP.

(2) Hydrogen flow control system comprised of an electronic D/P cell, an electronic recorder controller and an air operated control valve.

(3) New feed tank including liquid transfer lines to and from the slurry circulation pump.

(4) Load cell and digital readout - to monitor the weight of the feed tank and its contents.

(5) Temperature controllers for the high temperature heating tapes on the high pressure separators.

(6) Automated product let-down system for one high pressure separator.

(7) Magnedrive stirrer for the high pressure separator to be equipped with automatic product let-down.

(8) Recovery system for bottoms slurry from the hot high pressure separators.

The automated high pressure let-down system is comprised of a 55 $cm^3$ vessel positioned between two on/off air actuated valves which are operated sequentially. Because of the extremely abrasive nature of the slurry product and the high fluid velocities on let-down, 2-way angle valves with tungsten carbide stems and seats are used. The electronic circuits for the let-down system were designed at NSRFC to function with or without operational gamma ray level detection equipment.

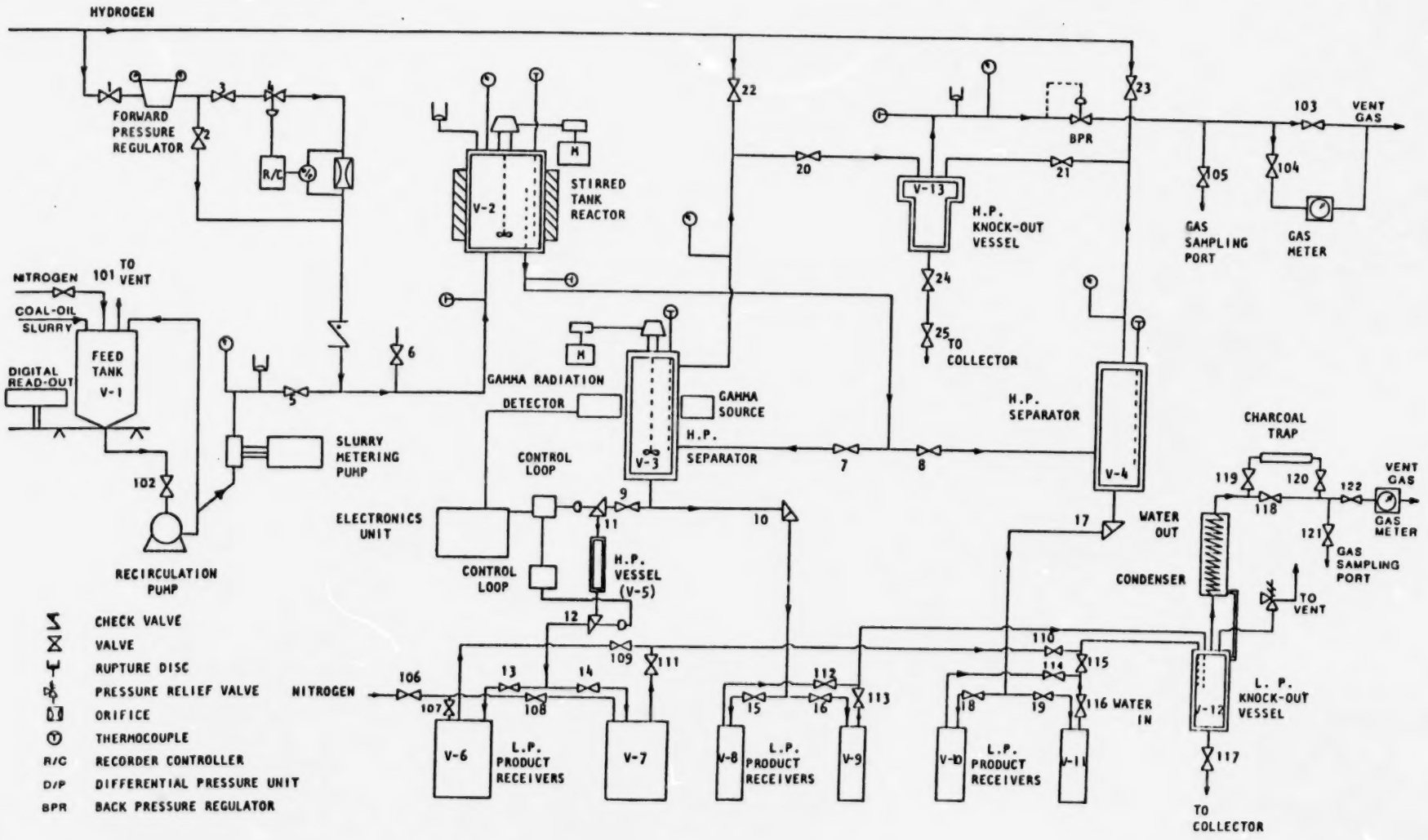
At present an intricate arrangement of timed relays is set manually to control the rate at which product is withdrawn from the bottom of the high pressure separator. This arrangement is being used because the gamma ray equipment designed to measure and control the liquid level is not fully operational. Difficulties encountered are related to the amplifier section of the Kay-Ray ion chamber detector. The manufacturer has recently supplied new electronic components for the system. These are currently being installed and will undergo testing in the near future. A detailed description of the automated let-down system is given in Appendix H.

## 5.1 Description of Continuous Coal Liquefaction Unit

A flowsheet of the bench-scale continuous coal liquefaction unit is presented in Figure 7. The unit is designed for high pressure (28 MPa) use and is suitable for processing 0.5 - 3.0 Kg per hour of coal oil slurry.

In the system, coal and oil are mixed batchwise in a 16-liter feed vessel. The coal oil slurry is continuously circulated by a rotary pump. This arrangement prevents settling of coal fines and provides suction pressure to the metering pump. Hydrogen is added and the mixture is fed to a 1500 $cm^3$ stirred tank reactor. The reactor is heated by a two-zone electric heater. Downstream of the reaction zone, products are passed to a hot separator. The overhead vapours and gases from the hot separator pass to a cold knock-out vessel. Light liquid products are condensed in the cold knock-out and a vent gas stream is provided through a back pressure regulator. The bottoms slurry from the hot separator is flashed at atmospheric pressure and collected. Vapours and gases from the low pressure product receivers are passed through a water-cooled knock-out vessel and condenser. Vent gas streams are monitored with gas meters.

Figure 7 - FLOWSHEET FOR CONTINUOUS COAL LIQUEFACTION UNIT



## 5.2 Results of Preliminary Trials

Modifications to the continuous coal liquefaction unit were scheduled to be completed by mid-January of 1982. Unfortunately, delays associated with the procurement and run-in of equipment rendered this schedule impossible. Alterations to the unit were near completion in May except for the installation of the automated product let-down system. Key components for this system, in particular the gamma ray equipment and the let-down valve trim sets, were not expected to arrive at NSRFC until late June. Progress was slow in acquiring these items due to prolonged communications with equipment suppliers and extended delivery times. Consequently, commissioning of the unit began late in May using a manual product let-down system. The automated let-down system was installed in September.

Commissioning trials were carried out varying reactor temperature, coal space velocity and hydrogen flowrate. Two coals were used during the trial runs. A Lingan coal containing 7% ash and a Prince coal with an ash content of 17%. In July a coal hydrogenation parameter study began. Very briefly, a series of twenty-four tests were planned according to a factorial design to investigate four potential critical parameters, temperature, pressure, coal space velocity and hydrogen treatrate. The concentration of coal in the feed slurry was fixed at 30 wt. %. Lingan coal was selected for this series of experiments. To ensure feedstock uniformity, an entire channel sample (approximately 60 Kg) was ground, screened to -200 mesh and mixed thoroughly. The ash content of this channel sample was 3%.

Conversion data for the three coals are presented in Table 12. A comparison of Run Nos. T-2, T-4 and 3001 shows that the conversions to THF solubles plus gases were quite similar, however, oil yields differ substantially. The highest yield of pentane soluble oil, 42.5%, was produced from the high ash Prince mine coal. Oil yields from the Lingan coals containing 3% and 7% ash were 30.4 and 34.7% respectively.

Figure 8 shows the effect of temperature on conversion of the Lingan 3% ash coal. The tests were carried out at 20.68 MPa and a slurry feedrate of 1 Kg/hr. Increasing the temperature from 425 to 460°C had no effect on conversion to THF solubles and gases. However, it is apparent from the data presented that oil yield increases and preasphaltenes decrease as temperature is raised from 425 to 450°C. Beyond 450°C the gas make continues to increase whereas oil yield changes little between 450 and 460°C.

The results of these experiments show that product yields vary significantly with feed coal. A comparison of product yields with the chemical analysis of the three coals suggest that conversion of coal to oil is a function of ash and/or sulphur contents. However, such a simple correlation could be misleading without consideration of other coal properties; e.g., rank and maceral composition. At this stage the scope of our continuous test program was reviewed. The program was revised to include an assessment of the effects of petrographic characteristics on conversion. Fresh channel samples were procured courtesy of the Cape Breton Development Corporation. Testing of these coals, Task 6, began in the fourth quarter of 1982.

TABLE 12

RESULTS OF PRELIMINARY CONTINUOUS COAL LIQUEFACTION TRIALS

| RUN NO. / COAL TESTED | T-2 LINGAN F | T-4 84% PRINCE B 16% LINGAN F | T-6 98% PRINCE B 2% LINGAN F | 3001 LINGAN G | 3002 LINGAN G | 3003 LINGAN G |
|---|---|---|---|---|---|---|
| A. OPERATING CONDITIONS | | | | | | |
| Unit Back Pressure, MPa | 20.68 | 20.68 | 20.68 | 20.68 | 20.68 | 20.68 |
| Temperatures, °C: | | | | | | |
| Reactor (Internal) | 450 | 450 | 450 | 450 | 425 | 460 |
| Slurry Preheater (Average) | 200 | 200 | 200 | 200 | 200 | 200 |
| Hot Separator | 229 | 232 | 248 | 231 | 247 | 256 |
| Feedrates: | | | | | | |
| Slurry, Kg/hr | 1.040 | 1.018 | 2.023 | 1.016 | 1.003 | 1.059 |
| Coal, Kg/hr | 0.312 | 0.305 | 0.607 | 0.305 | 0.301 | 0.318 |
| Hydrogen, L/hr | 247. | 299. | 301. | 320. | 335. | 335. |
| Hydrogen Treatrate, Wt. % Dry Coal | 7.0 | 9.0 | 4.5 | 9.6 | 10.2 | 9.7 |
| Hours on Stream | 8.2 | 8.9 | 7.3 | 8.9 | 6.0 | 6.1 |
| B. CONVERSIONS, WT. % OF maf COAL | | | | | | |
| Pentane Solubles plus Gases | 42.9 | 53.4 | 44.3 | 39.9 | 27.1 | 41.1 |
| Benzene Solubles plus Gases | 68.1 | 76.6 | 69.1 | 64.6 | 52.6 | 68.6 |
| THF Solubles plus Gases | 86.1 | 90.4 | 89.5 | 87.9 | 86.9 | 87.1 |
| C. PRODUCT DISTRIBUTION, WT. % OF maf COAL | | | | | | |
| $CH_4$ | 2.3 | 2.4 | 0.9 | 2.8 | 1.3 | 4.0 |
| $C_2H_6$ | 1.7 | 2.3 | 0.9 | 2.3 | 1.0 | 3.4 |
| $C_3H_8$ | 1.4 | 2.6 | 0.7 | 1.7 | 0.6 | 2.3 |
| $C_4H_{10}$ | 1.2 | 1.2 | 0.5 | 1.5 | 0.8 | 1.8 |
| CO | 0.9 | 0.4 | 0.2 | 0.3 | 0.2 | 0.4 |
| $H_2S$ | 0.7 | 2.0 | 1.2 | 0.4 | 0.4 | 0.3 |
| $H_2O$ | - - | - - | - - | 0.5 | 0.6 | 0.7 |
| Oil | 34.7 | 42.5 | 39.9 | 30.4 | 22.2 | 28.2 |
| Asphaltenes | 25.2 | 23.2 | 24.8 | 24.7 | 25.5 | 27.5 |
| Preasphaltenes | 18.0 | 13.8 | 20.4 | 23.3 | 34.3 | 18.5 |
| Unreacted Coal | 13.9 | 9.6 | 10.5 | 12.1 | 13.1 | 12.9 |
| D. $H_2$ CONSUMPTION, WT. % OF maf COAL | 1.9 | 3.0 | 2.4 | 2.2 | 1.5 | 2.4 |
| E. MATERIAL BALANCE CLOSURE, % | 101.5 | 98.0 | 95.6 | 97.9 | 99.4 | 97.4 |

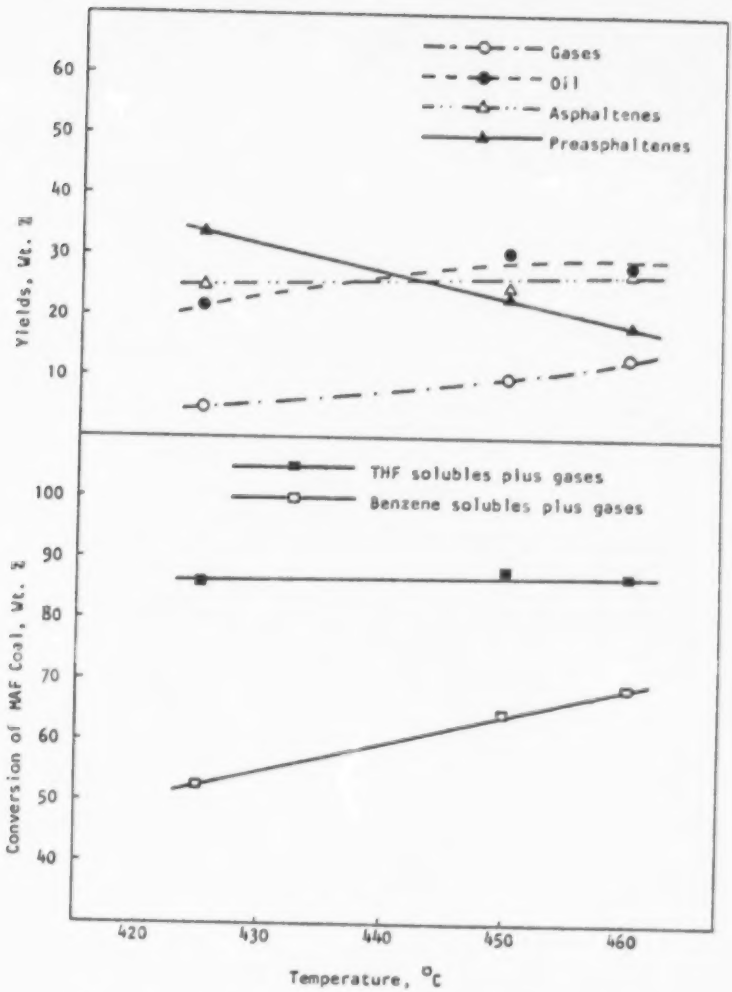



Figure 8 - EFFECT OF TEMPERATURE ON CONVERSION OF LINGAN COAL

## TASK 6 - CONTINUOUS DONOR SOLVENT LIQUEFACTION OF SYDNEY AREA COALS

The principal objective of this task was to investigate donor solvent liquefaction of coals from the Sydney coalfield in a continuous bench-scale unit. The test program was designed to study the effects of operating conditions and coal properties on yield structures. A total of twenty-four runs were carried out using the continuous coal hydrogenation unit shown in Figure 7. Channel samples of Harbour and Hub seam coals were included in the test program. Harbour seam samples were obtained from Lingan and No. 26 collieries, Hub seam samples from the Prince mine.

### 6.1 Coal Hydrogenation Parameter Study

A series of sixteen experiments were carried out according to a factorial design to evaluate the effects of coal feedstock, reaction temperature, operating pressure and slurry feedrate on product composition. Prince Batch D and Lingan Batch K were used for this coal hydrogenation parameter study. Hydrogenated anthracene oil containing 9.1% H was used as the donor vehicle. The concentration of coal in the feed slurry was fixed at 30 wt. %. Hydrogen treatrate was ca. 7.5 wt. % based on dry coal. The operating conditions investigated were as follows:

| | |
|---|---|
| Reactor Temperature, $^{o}C$ | 440, 460 |
| Back Pressure, MPa | 17.24, 20.68 |
| Slurry Feedrate, Kg/hr | 1, 2. |

At a slurry feedrate of 1 Kg/hr the average residence time of coal particles in the reaction zone is estimated to be 42 minutes.

This estimate is based on the physical properties of the vehicle oil at operating conditions. The physical data required was developed experimentally. The average residence time of coal particles in the reaction zone at a slurry feedrate of 2 Kg/hr is estimated to be 21 minutes.

A typical continuous liquefaction run was of 6 hours duration. However, an additional 5-6 hours was required for preliminary and post run operations. In the majority of runs the controlled variables lined-out about 4 hours after start-up. During the steady state operating period vent gas streams were sampled and other product streams were collected for analytical and material balance purposes. A detailed operating procedure is given in Appendix G.

In these experiments the following definitions for the product fractions isolated by solvent extraction were used:

Oil - pentane solubles

Asphaltenes - benzene solubles, pentane insolubles.

Preasphaltenes - THF solubles, benzene insolubles.

A Direct extraction technique was used to determine these fractions. Individual samples of product slurry were separately extracted with pentane, benzene, and tetrahydrofuran (THF). Conversions were calculated on the basis of maf coal fed to the reactor during the steady state sampling period and unconverted coal in the dry insoluble residues. Conversion calculations are described in Appendix A.

Vent gas streams were analyzed using a Perkin-Elmer Sigma 3B gas chromatograph interfaced with a Perkin-Elmer Sigma 10 chromatography data station. Simulated distillations were also done with this instrumentation using the D-2887 Sigma Basic program.

Table 13 summarizes the results of the coal hydrogenation parameter study. An examination of the data indicates that the controlled variables studied certainly do effect product distribution. A statistical evaluation of the data was carried out to determine the significance of the observed effects. The response variables selected for the statistical analysis included gas make, oil yield, asphaltenes, preasphaltenes and hydrogen consumption. A standard analysis of variance was used to establish confidence levels. Details are presented in Appendix E.

Temperature was found to have a significant effect on the conversion of coal to the products listed. Increasing the operating temperature from 440 to 460°C produced higher yields of gases and oil and lower yields of asphaltenes and preasphaltenes. For example, a comparison of Run No. 3116 at 440°C and Run No. 3111 at 460°C shows the following shift in product distribution:

- Gases increased from 9.3 to 13.3%
- Oil increased from 24.7 to 30.8%.
- Asphaltenes decreased from 29.8 to 25.1%
- Preasphaltenes decreased from 20.5 to 16.1%.

TABLE 13

SUMMARY OF RESULTS FROM COAL HYDROGENATION PARAMETER STUDY
USING CONTINUOUS-FLOW UNIT

| RUN NO. | 3110 | 3112 | 3114 | 3116 | 3115 | 3117 | 3118 | 3111 |
|---|---|---|---|---|---|---|---|---|
| Temperature, °C | 440 | 440 | 440 | 440 | 460 | 460 | 460 | 460 |
| Back Pressure, MPa | 20.68 | 17.24 | 20.68 | 17.24 | 20.68 | 17.24 | 20.68 | 17.24 |
| Slurry Feedrate, Kg/hr | 1.034 | 0.995 | 1.968 | 2.039 | 1.017 | 0.982 | 2.020 | 2.060 |
| $H_2$ Consumption, Wt. % maf Coal | 1.6 | 1.3 | 1.6 | 1.1 | 2.0 | 1.7 | 1.6 | 1.3 |
| CONVERSIONS, WT. % OF maf COAL | | | | | | | | |
| Pentane Solubles plus Gases | 43.9 | 43.1 | 35.8 | 34.0 | 50.7 | 50.1 | 45.2 | 44.1 |
| Benzene Solubles plus Gases | 71.1 | 71.3 | 64.4 | 63.8 | 76.5 | 75.7 | 70.4 | 69.2 |
| THF Solubles plus Gases | 87.1 | 86.9 | 84.9 | 84.3 | 88.4 | 87.9 | 86.9 | 85.3 |
| PRODUCT DISTRIBUTION, WT. % OF maf COAL | | | | | | | | |
| Gases | 9.8 | 12.1 | 8.5 | 9.3 | 17.7 | 20.4 | 12.9 | 13.3 |
| Oil | 34.1 | 31.0 | 27.3 | 24.7 | 33.0 | 29.7 | 32.3 | 30.8 |
| Asphaltenes | 27.2 | 28.2 | 28.6 | 29.8 | 25.8 | 25.6 | 25.2 | 25.1 |
| Preasphaltenes | 16.0 | 15.6 | 20.5 | 20.5 | 11.9 | 12.2 | 16.5 | 16.1 |

Prince coal (Batch D) used for Run Nos. 3110 - 3118 inclusive.
Coal concentration in feed slurry: 30 wt. %.
Detailed product distribution given in Appendix B.

TABLE 13 (CONTINUED)

SUMMARY OF RESULTS FROM COAL HYDROGENATION PARAMETER STUDY
USING CONTINUOUS-FLOW UNIT

| RUN NO. | 3129 | 3127 | 3126 | 3124 | 3125 | 3123 | 3122 | 3128 |
|---|---|---|---|---|---|---|---|---|
| Temperature, °C | 440 | 440 | 440 | 440 | 460 | 460 | 460 | 460 |
| Back Pressure, MPa | 20.68 | 17.24 | 20.68 | 17.24 | 20.68 | 17.24 | 20.68 | 17.24 |
| Slurry Feedrate, Kg/hr | 0.999 | 1.042 | 2.020 | 1.984 | 1.038 | 1.087 | 1.996 | 2.045 |
| $H_2$ Consumption, Wt. % maf Coal | 1.4 | 1.0 | 1.4 | 1.0 | 1.4 | 1.3 | 1.4 | 1.4 |
| CONVERSIONS, WT. % OF maf COAL | | | | | | | | |
| Pentane Solubles plus Gases | 30.0 | 33.0 | 24.2 | 24.8 | 41.0 | 42.2 | 35.0 | 35.5 |
| Benzene Solubles plus Gases | 59.9 | 60.7 | 52.0 | 52.9 | 67.7 | 68.4 | 61.6 | 60.8 |
| THF Solubles plus Gases | 85.7 | 85.8 | 83.2 | 81.9 | 87.1 | 86.5 | 84.9 | 85.5 |
| PRODUCT DISTRIBUTION, WT. % OF maf COAL | | | | | | | | |
| Gases | 9.4 | 9.3 | 6.8 | 7.2 | 14.8 | 16.0 | 11.3 | 12.2 |
| Oil | 20.6 | 23.7 | 17.4 | 17.6 | 26.2 | 26.2 | 23.7 | 23.3 |
| Asphaltenes | 29.9 | 27.7 | 27.8 | 28.1 | 26.7 | 26.2 | 26.6 | 25.3 |
| Preasphaltenes | 25.8 | 25.1 | 31.2 | 29.0 | 19.4 | 18.1 | 23.3 | 24.7 |

Lingan coal (Batch K) used for Run Nos. 3122 - 3129 inclusive.
Coal concentration in feed slurry; 30 wt. %.
Detailed product distribution given in Appendix B.

The effect of pressure was only significant with regard to gas make and hydrogen consumption. Increasing the operating pressure from 17.24 to 20.68 MPa had a negative effect on gas make and a positive effect on hydrogen consumption. For example, in Run No. 3117 at 17.24 MPa the gas make was 20.4% compared with 17.7% in Run No. 3115 at 20.68 MPa. Furthermore, the hydrogen consumption in Run No. 3117 was 1.7% compared with 2.0% in Run No. 3115.

Slurry feedrate was found to significantly affect the yields of gases, oil and preasphaltenes. Increasing the slurry feedrate produced lower yields of gases and oil and higher yields of preasphaltenes. A comparison of Run No. 3112 at 1 Kg/hr and Run No. 3116 at 2 Kg/hr shows the following shift in product distribution:

- gases decrease from 12.1 to 9.3%
- oil decreases from 31.0 to 24.7%
- preasphaltenes increase from 15.6 to 20.5%.

The statistical evaluation shows that coal feedstock significantly affects product distribution and hydrogen consumption. Continuous runs with the Prince Batch D coal produced higher gas makes, higher oil yields and lower yields of preasphaltenes than runs with the Lingan Batch K coal at similar operating conditions. In general, hydrogen consumption was higher with the Prince mine coal. The following comparison illustrates the effect of coal feedstock on yields and hydrogen consumption:

| | RUN NO. 3115 PRINCE BATCH D | RUN NO. 3125 LINGAN BATCH K |
|---|---|---|
| Products, Wt. % | | |
| Gases | 17.7 | 14.8 |
| Oil | 33.0 | 26.2 |
| Asphaltenes | 25.8 | 26.7 |
| Preasphaltenes | 11.9 | 19.4 |
| Hydrogen Consumption, Wt. % | 2.0 | 1.4 |

Analysis of the benzene soluble fractions from these experiments are presented in Appendix D. As expected, the elemental compositions and the simulated distillations reflect the degree of processing severity.

## 6.2 Dependence of Liquefaction Behavior on Coal Properties

In addition to the feedstocks used in the coal hydrogenation parameter study four other coals were tested (Prince Batch C, Lingan Batch I, Lingan Batch J and No. 26 Batch B). Continuous experiments were carried out at operating conditions judged best to maximize oil yield. Results are presented in Table 14. The product distributions show that oil yield varied from 21.0 to 29.6% and product preasphaltenes ranged from 13.4 to 23.7%. Conversions for the Lingan coals were

TABLE 14

PRODUCT DISTRIBUTIONS FROM CONTINUOUS EXPERIMENTS
WITH PRINCE, LINGAN AND NO. 26 COLLIERY COALS

| RUN NO. | 3119 | 3120 | 3131 | 3132 | 3133 | 3134 | 3135 | 3136 |
|---|---|---|---|---|---|---|---|---|
| Coal Tested: | Prince Batch C | | Lingan Batch J | | Lingan Batch I | | No. 26 Batch B | |
| Temperature, °C | 460 | 450 | 460 | 460 | 460 | 460 | 460 | 460 |
| Back Pressure, MPa | 17.24 | 17.24 | 17.24 | 17.24 | 20.68 | 20.68 | 20.68 | 20.68 |
| Slurry Feedrate, Kg/hr | 1.022 | 1.025 | 1.029 | 1.007 | 1.072 | 1.005 | 1.031 | 0.995 |
| $H_2$ Consumption, Wt. % maf Coal | 1.5 | 1.1 | 1.8 | 1.5 | 1.5 | 1.2 | 1.3 | 1.1 |
| CONVERSIONS, WT. % OF maf COAL: | | | | | | | | |
| Pentane Solubles plus Gases | 47.3 | 45.1 | 47.0 | 45.1 | 41.8 | 44.0 | 36.3 | 37.0 |
| Benzene Solubles plus Gases | 73.7 | 70.5 | 71.7 | 71.3 | 67.3 | 68.9 | 61.4 | 62.8 |
| THF Solubles plus Gases | 87.1 | 86.5 | 89.4 | 88.9 | 87.0 | 87.7 | 85.1 | 85.7 |
| PRODUCT DISTRIBUTION, WT. % OF maf COAL | | | | | | | | |
| Gases | 20.0 | 15.6 | 17.4 | 18.6 | 15.6 | 17.0 | 15.3 | 15.9 |
| Oil | 27.3 | 29.5 | 29.6 | 26.5 | 26.2 | 27.0 | 21.0 | 21.1 |
| Asphaltenes | 26.4 | 25.4 | 24.7 | 26.2 | 25.5 | 24.9 | 25.1 | 25.8 |
| Preasphaltenes | 13.4 | 16.0 | 17.7 | 17.6 | 19.7 | 18.8 | 23.7 | 22.9 |

Coal concentration in feed slurry; 30 wt. %.
Detailed product distribution given in Appendix B.

quite similar although the product distribution for Lingan Batch J appeared to be marginally better in Run No. 3131. Run No. 3135 made with No. 26 colliery coal produced the lowest oil yield, 21.0%, and the highest yield of preasphaltenes, 23.7%.

It is well recognized that the liquefaction behavior of a coal is dependent on both its chemical and petrographic characteristics (85, 86). Figures 9 - 15 are presented to illustrate the variation of conversion with individual coal properties.

Figures 9 and 10 indicate that pyritic and organic sulphur both have a positive influence on coal conversion. At higher concentrations of these constituents oil yield is enhanced and there is a substantial decrease in the preasphaltenes fraction. A similar trend is apparent for ash content as shown in Figure 12.

The influence of carbon content on conversion is presented in Figure 13. The highest conversions to benzene solubles plus gases were found for coals with 73-78% carbon. Plotting conversion against vitrinite content, Figure 14, gave scattered points for coals containing 74-81 volume % vitrinite. Since five of the six points were in that region no correlation was drawn. The effect of coal rank on conversion is shown in Figure 15. Coal rank is presented in terms of maximum reflectance of vitrinite (% $R_o$ max.). Figure 15 shows that the degree of conversion to benzene solubles plus gases increases significantly as rank decreases. The highest oil yield, 33%, was produced from Prince low rank coal, 0.78% $R_o$ max.

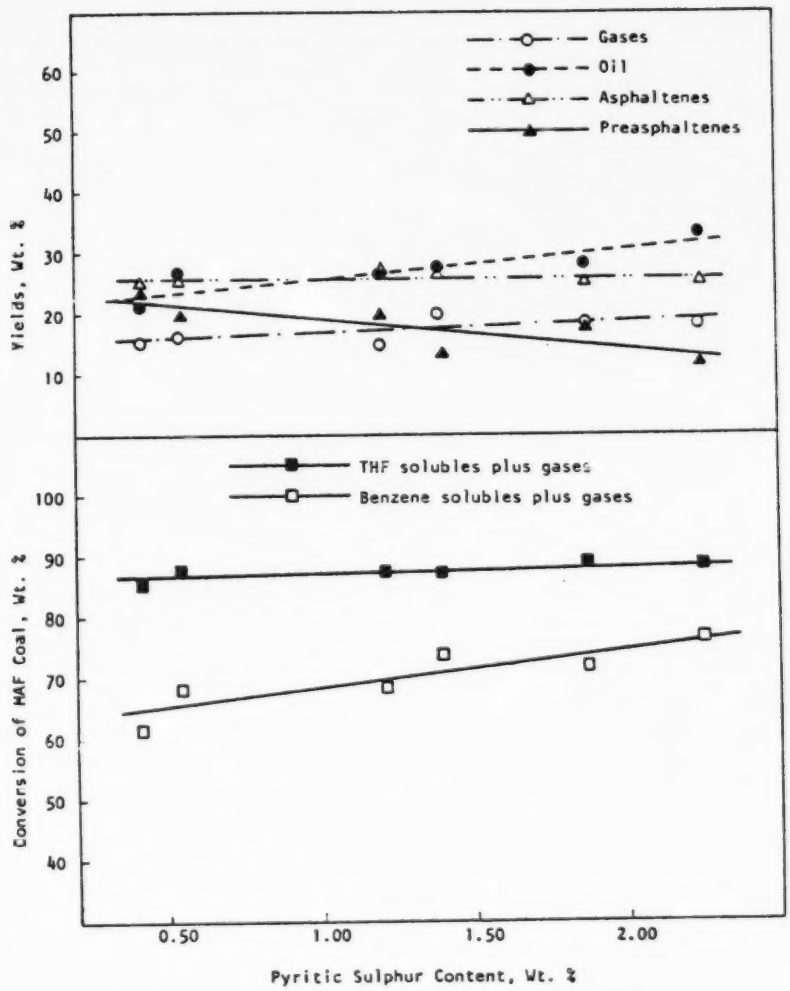



Figure 9 - INFLUENCE OF PYRITIC SULPHUR CONTENT ON COAL CONVERSION

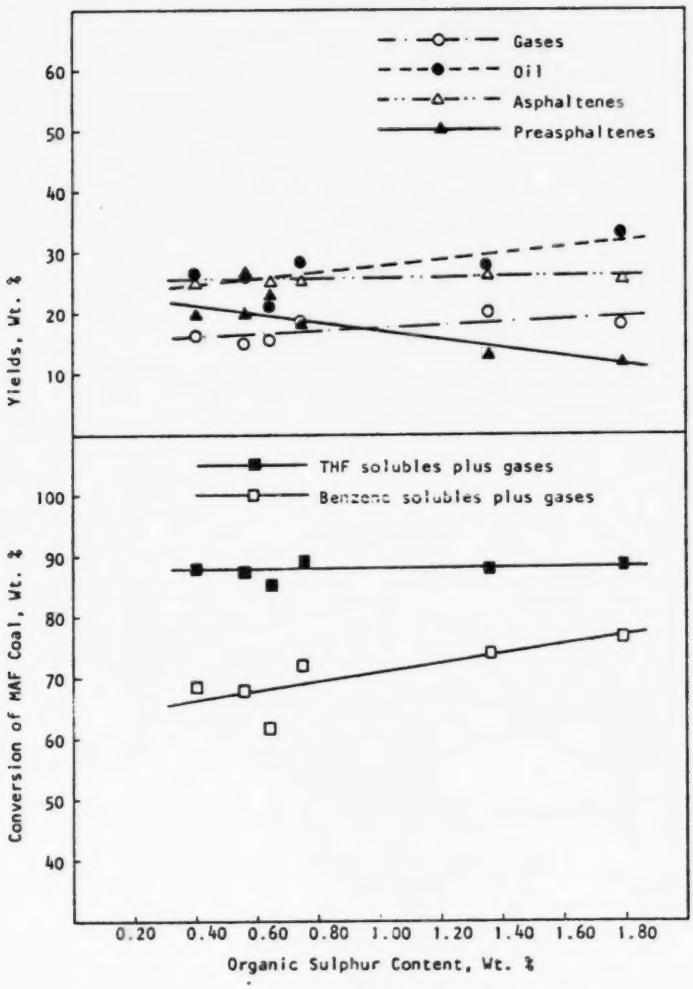



Figure 10 - COAL CONVERSION AS A FUNCTION OF ORGANIC SULPHUR CONTENT

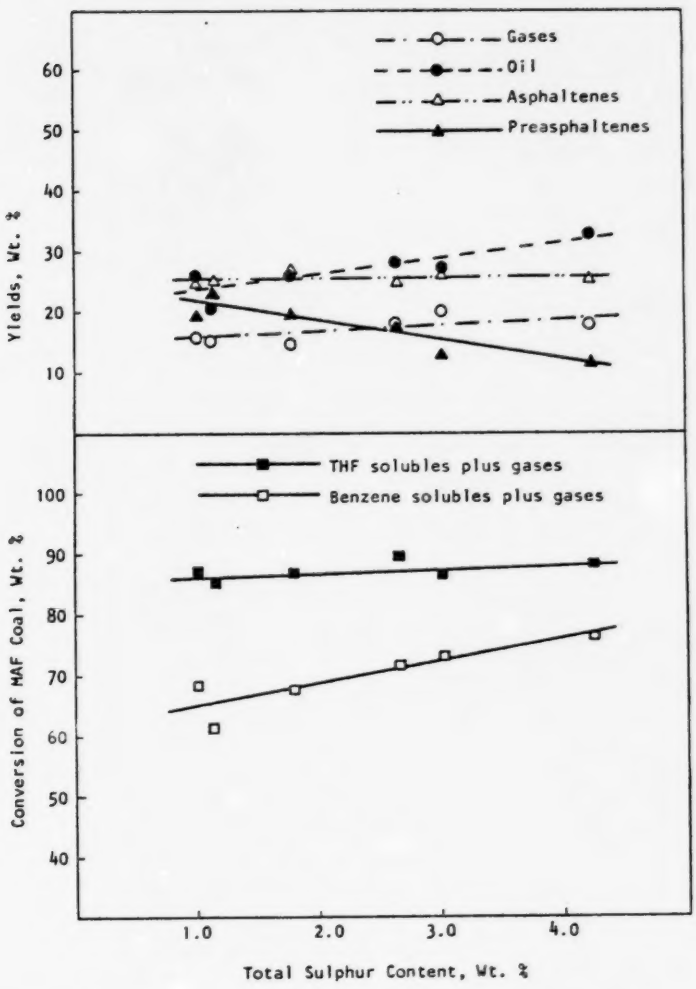



Figure 11 - VARIATION OF COAL CONVERSION WITH TOTAL SULPHUR CONTENT

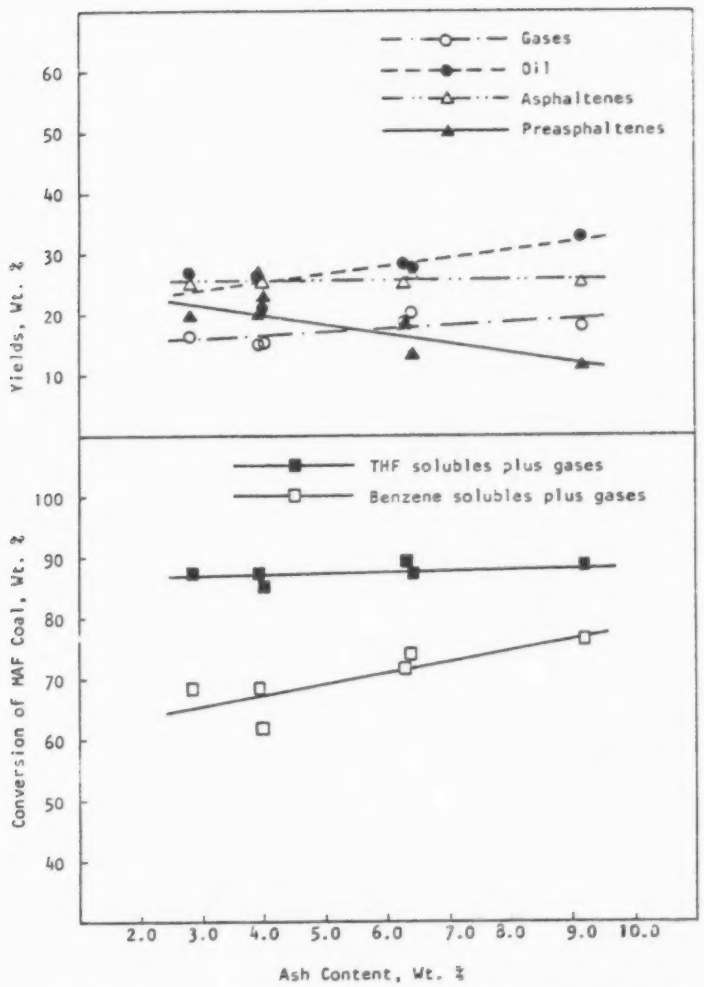



Figure 12 - EFFECT OF ASH CONTENT ON COAL CONVERSION

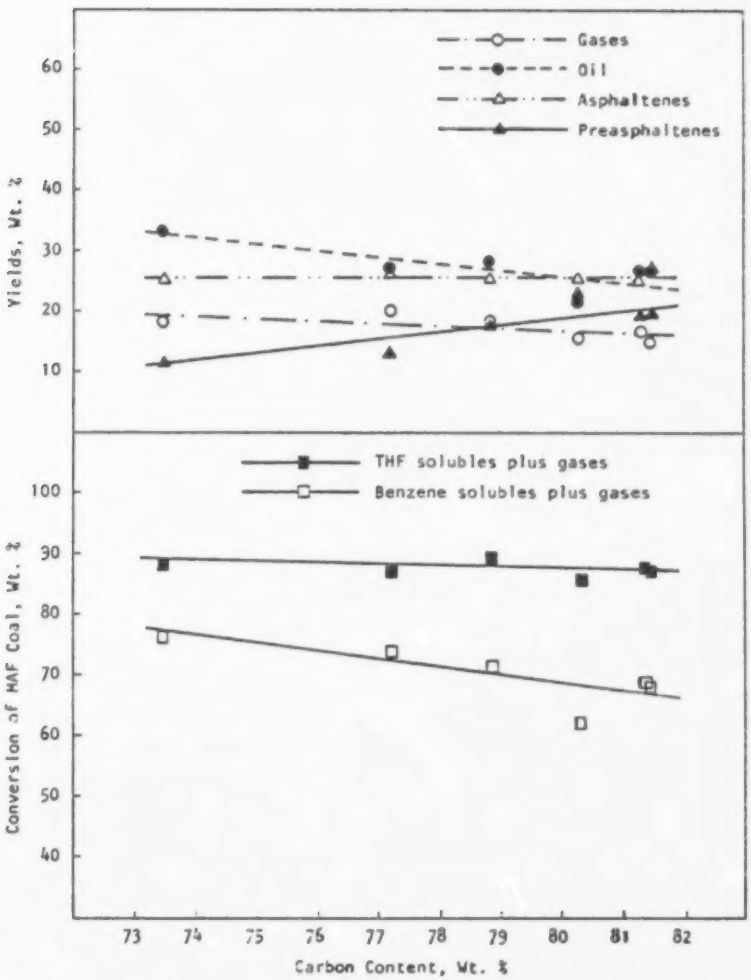



Figure 13 - INFLUENCE OF CARBON CONTENT ON COAL CONVERSION

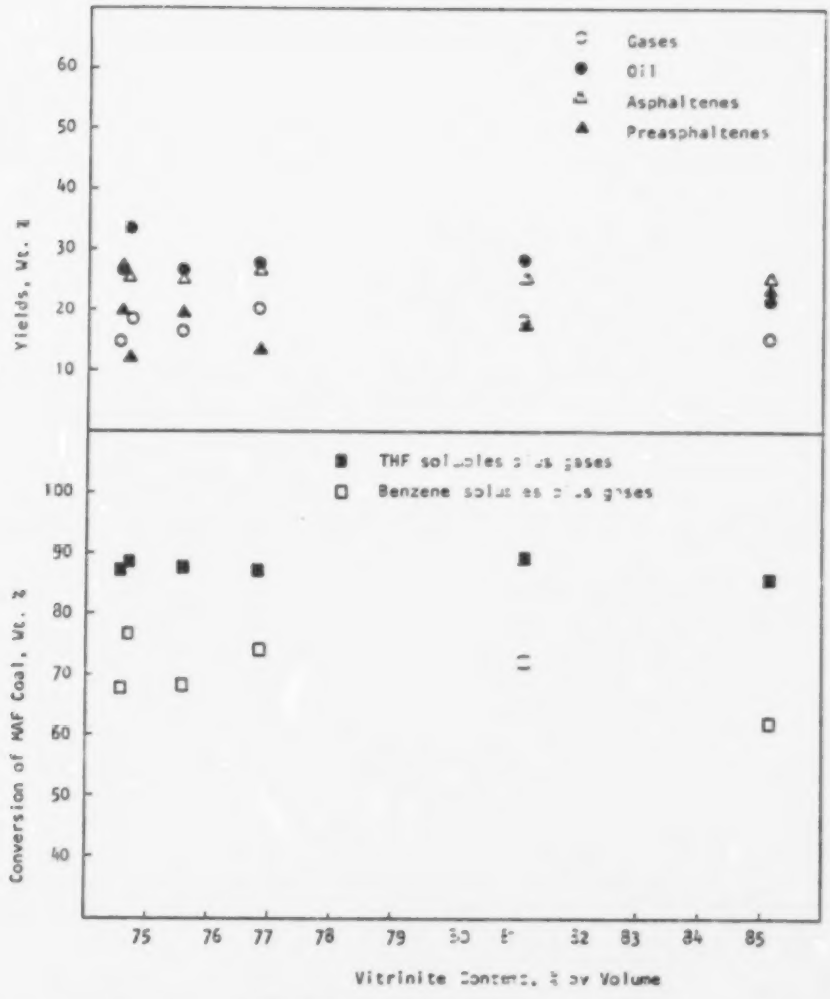



Figure 14 - VARIATION OF COAL CONVERSION WITH VITRINITE CONTENT

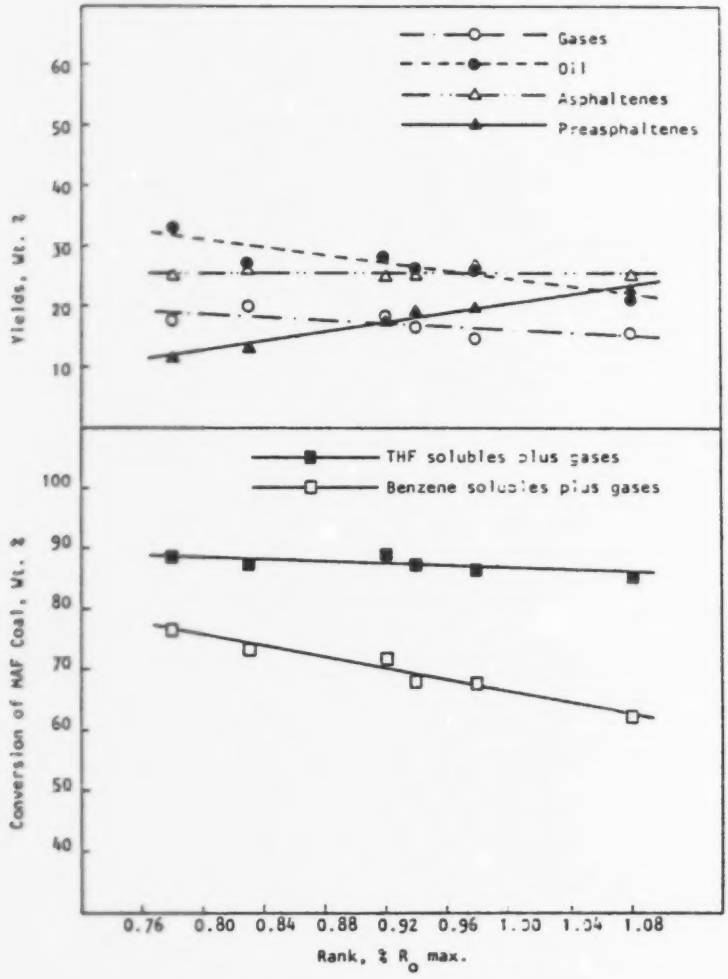



Figure 15 - EFFECT OF RANK ON COAL CONVERSION

Although Figures 9 - 15 suggest that simple correlations exist between coal conversion and individual coal properties, it must be kept in mind that conversion is influenced by several properties interacting simultaneously. For example, the optimum oil yield achieved with Prince mine coal was affected by the positive influences of ash, sulphur and coal rank. A comparison of Prince coal with No. 26 colliery coal shows that the latter has lower levels of ash and sulphur and is of higher rank. Hence, No. 26 coal gave a lower oil yield than the Prince coals tested.

On the basis of rank one would expect Prince coal to give higher oil yields than Lingan coal. However, Run Nos. 3131 and 3132 with Lingan Batch J produced about the same oil yield, 28%, as Run No. 3119 with Prince Batch C. An examination of proximate and ultimate analysis shows that the two coals had similar ash and sulphur contents. Furthermore, the petrographic analysis show that although the Prince sample did have a slightly lower vitrinite reflectance, the Lingan sample had a slightly higher vitrinite content. In conclusion, coals from the Sydney coalfield vary in their reactivity at thermal liquefaction conditions depending on several coal properties. The critical chemical and petrographic characteristics have been identified.

## 6.3 Recovery of Coal Liquids

The purpose of this work was to establish distillable liquid yield employing a combination of vacuum distillation and coking as a separation step following liquefaction. Separator bottoms (product slurry) from selected continuous thermal liquefaction experiments were

processed in this study. A simplified flow diagram of the apparatus used is shown in Figure 16.

In this series of batch experiments an 800g sample of separator bottoms was charged to the 3500 $cm^3$ stainless steel coking vessel. The system was evacuated for fifteen minutes, then a nitrogen purge was set to maintain a working pressure of ca. 2 kPa. At this point the furnace was activated. The total heat-up time ranged from 60-70 minutes depending on the desired coking temperature. The duration of the coking cycle was 45 minutes. Distillate yields were calculated on the basis of maf coal processed during the steady state sampling period of the liquefaction step.

Table 15 summarizes the results of the vacuum distillation/coking runs. Preliminary trials established the optimum coking temperature to be 425°C. In all cases distillate yields were found to be lower than the oil yields determined by solvent analysis. For example, in Run No. 3120 the distillate yield was 26.6% whereas the conversion of maf coal to pentane soluble oil was 29.5%. These results are not surprising, however, taking the following points into consideration:

(a) Distillate yields were calculated on the assumption that vehicle oil output equals vehicle oil input. Hence, distillate yield is *net* product oil allowing for the loss of vehicle oil due to cracking.

(b) Water cooling alone is not adequate for the recovery of light ends, in particular $C_5$'s.

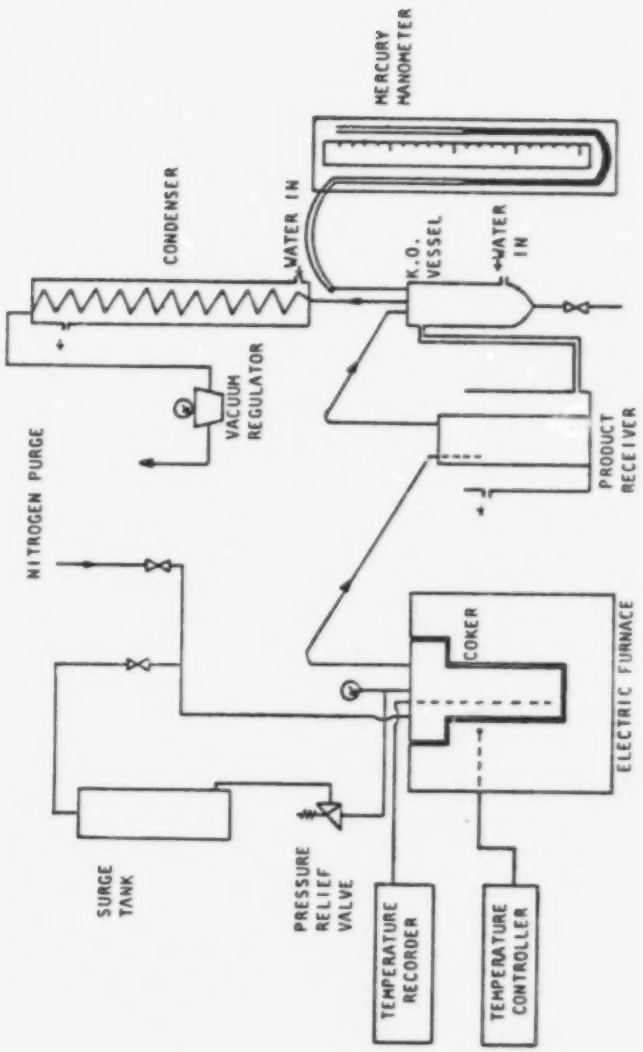



Figure 16 - SIMPLIFIED FLOW DIAGRAM OF VACUUM DISTILLATION/COKING APPARATUS

TABLE 15

RESULTS OF BATCH VACUUM DISTILLATION/COKING EXPERIMENTS

| COKER RUN NO. | 83-119 | 83-120 | 83-117 | 83-115 | 83-134 | 83-131 | 83-125 | 83-135 |
|---|---|---|---|---|---|---|---|---|
| FEED: Separator Bottoms | Run No. 3119 | Run No. 3120 | Run No. 3117 | Run No. 3115 | Run No. 3134 | Run No. 3131 | Run No. 3125 | Run No. 3135 |
| Coal Processed | Prince Batch C | Prince Batch C | Prince Batch D | Prince Batch D | Lingan Batch I | Lingan Batch J | Lingan Batch K | No. 26 Batch B |
| COKING TEMPERATURE, °C | 350 | 425 | 475 | 425 | 425 | 425 | 425 | 425 |
| OPERATING PRESSURE, kPa | 1.86 | 2.00 | 2.13 | 1.86 | 2.13 | 2.27 | 2.27 | 2.13 |
| DISTILLATE YIELD, WT. % OF MAF COAL | 12.4 | 26.6 | 26.4 | 31.5 | 21.6 | 22.2 | 21.3 | 16.8 |
| ANALYSIS OF DISTILLATE: | | | | | | | | |
| Carbon, Wt. % | 89.33 | 90.75 | 90.72 | 90.89 | 91.07 | 91.60 | 91.05 | 91.43 |
| Hydrogen, Wt. % | 8.11 | 8.29 | 8.42 | 8.45 | 8.34 | 8.31 | 8.60 | 8.40 |
| Nitrogen, Wt. % | 0.20 | 0.22 | 0.21 | 0.26 | 0.21 | 0.21 | 0.22 | 0.22 |
| Sulphur, Wt. % | 0.054 | 0.070 | 0.065 | 0.060 | 0.025 | 0.036 | 0.027 | 0.028 |
| Distillation Data, °C (Simulated by Gas Chromatography) | | | | | | | | |
| IBP/5 | | 167/207 | | 162/206 | 161/206 | 157/206 | 158/206 | 161/207 |
| 10/30 | | 233/285 | | 229/280 | 232/284 | 230/281 | 232/283 | 234/283 |
| 50 | | 313 | | 312 | 312 | 312 | 313 | 314 |
| 70/90 | | 346/389 | | 338/381 | 339/383 | 338/382 | 341/385 | 341/386 |
| 95/EP | | 421/487 | | 414/482 | 414/481 | 415/482 | 419/484 | 423/491 |

TABLE 16

ANALYSIS OF PENTANE-SOLUBLE FRACTIONS FROM CONTINUOUS COAL LIQUEFACTION TESTS

| RUN NO.<br>COAL TESTED: | 3115<br>Prince<br>Batch D | 3120<br>Prince<br>Batch C | 3125<br>Lingan<br>Batch K | 3131<br>Lingan<br>Batch J | 3134<br>Lingan<br>Batch I | 3135<br>No. 26<br>Batch B |
|---|---|---|---|---|---|---|
| Carbon, Wt. % | 90.22 | 90.10 | 91.00 | 90.49 | 90.20 | 91.51 |
| Hydrogen, Wt. % | 8.21 | 8.15 | 8.37 | 8.05 | 8.12 | 8.36 |
| Nitrogen, Wt. % | 0.24 | 0.20 | 0.21 | 0.22 | 0.21 | 0.20 |
| Sulphur, Wt. % | 0.065 | 0.074 | 0.031 | 0.046 | 0.031 | 0.026 |
| Distillation Data, °C<br>(Simulated by Gas Chromatography) | | | | | | |
| IBP/5 | 166/208 | 168/207 | 162/207 | 163/207 | 157/207 | 159/208 |
| 10/30 | 232/281 | 233/283 | 231/281 | 232/281 | 229/281 | 237/282 |
| 50 | 312 | 312 | 312 | 312 | 313 | 313 |
| 70/90 | 340/379 | 345/387 | 343/386 | 344/390 | 345/390 | 343/387 |
| 95/EP | 407/477 | 417/482 | 418/488 | 427/493 | 427/487 | 420/485 |

(c) The duration of the steady state sampling period was short. This tends to enlarge the effect of material losses, due to hold-up in transfer lines and/or knock-out vessels, on product oil yields.

Several of the liquids recovered from the coker runs were analyzed along with pentane soluble fractions from the liquefaction experiments, Tables 15 and 16. It is evident from the data that the coker distillates and the pentane soluble fractions have similar elemental compositions and boiling point ranges.

### 6.4 Mechanisms of Hydrogen Transfer in Donor Solvent Liquefaction of Coal

As mentioned earlier in this report the conversion of coal to liquid products by direct hydroliquefaction is highly dependent on the stabilization of pyrolytically formed free-radicals. These highly reactive free-radicals are normally stabilized by accepting hydrogen. Thus in donor solvent liquefaction a structural requirement of the vehicle is that it contains transferable hydrogen. Hydroaromatic compounds such as tetralin have been identified as effective hydrogen donor vehicles for coal dissolution.

In this study proton NMR spectroscopy was used to assess the hydroaromaticity of solvents prepared from raw anthracene oil. H-NMR spectra were obtained using a Varian CFT-20 NMR spectrometer operating in the Fourier transform mode at 80 MHz and a Nicolet 360NB NMR spectrometer operating in the Fourier transform mode at 360 MHz. In both cases tetramethylsilane was used as internal reference and

peak areas were integrated electronically using software routines supplied by the manufacturers. Proton assignments were as follows: aromatic hydrogens ($H_{ar}$) are found in the region 9-6 ppm. Benzylic hydrogens, including methyls, occur at 3.5 to 2 ppm ($H_{\alpha}$). Hydrogens, except methyls, on carbons one or more positions removed from aromatic rings, occur at 2-1.1 ppm ($H_{\beta}$). Aliphatic methyls are found at 1.1-0.4 ppm ($H_{\gamma}$). As almost no long aliphatic side chains are believed to be present, the $H_{\beta}$ protons are predominantly in rings. These assignments are consistent with similar analysis reported in the literature (87, 88).

Raw anthracene oil is highly aromatic as shown in Table 17. However, on hydrogenation the concentration of $H_{\beta}$ (characteristic of tetralin or similar hydroaromatics) increases dramatically. Batch autoclave experiments with the three hydrogenated solvents (HAO 1, HAO 2 and HAO 4) showed HAO 4 to be the most effective solvent for conversion of Lingan mine coal.

Table 18 presents hydrogen distribution data for HAO 4 and various liquefaction product fractions from Run Nos. 3115, 3125 and 3135. The actual weight per cent of each type of hydrogen was calculated from the total hydrogen content and the normalized proton distribution established by H-NMR. Even though the product liquids are diluted due to the presence of vehicle oil, these data show that the product liquids are high in aromatic hydrogen. Furthermore, the depletion of $\beta$ hydrogen relative to $\alpha$ and $\gamma$ hydrogen in the benzene soluble fractions indicates that $\beta$ hydrogen is transferable during liquefaction.

TABLE 17

PROTON DISTRIBUTIONS FOR RAW AND HYDROGENATED ANTHRACENE OIL

| SAMPLE DESCRIPTION | TOTAL HYDROGEN CONTENT (wt. %) | PROTON DISTRIBUTION (%) | | | |
|---|---|---|---|---|---|
| | | $H_{ar}$ | $H_{\alpha}$ | $H_{\beta}$ | $H_{\gamma}$ |
| Raw Anthracene Oil | 5.70 | 89.22 | 7.84 | 1.96 | 0.98 |
| HAO 1 | 6.42 | 68.01 | 20.16 | 9.91 | 1.92 |
| HAO 2 | 7.64 | 47.20 | 23.20 | 21.60 | 8.00 |
| HAO 4 | 9.05 | 26.95 | 24.11 | 38.30 | 10.64 |

TABLE 18

H-NMR ANALYSIS OF VARIOUS LIQUEFACTION PRODUCT FRACTIONS

| SAMPLE DESCRIPTION | | TOTAL HYDROGEN CONTENT (WT. %) | PROTON DISTRIBUTION (%) | | | | $H_{ar}$ CONTENT (WT. %) | $H_{\alpha}$ CONTENT (WT. %) | $H_{\beta}$ CONTENT (WT. %) | $H_{\gamma}$ CONTENT (WT. %) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $H_{ar}$ | $H_{\alpha}$ | $H_{\beta}$ | $H_{\gamma}$ | | | | |
| HAO 4 | | 9.05 | 26.95 | 24.11 | 38.30 | 10.64 | 2.44 | 2.18 | 3.47 | 0.96 |
| RUN NO. 3115: | Pentane Soluble Fraction | 8.21 | 38.01 | 23.36 | 31.15 | 7.48 | 3.12 | 1.92 | 2.56 | 0.61 |
| | Benzene Soluble Fraction | 7.83 | 41.94 | 21.77 | 29.03 | 7.26 | 3.28 | 1.71 | 2.27 | 0.57 |
| | THF Soluble Fraction | 7.79 | 43.35 | 23.12 | 27.75 | 5.78 | 3.38 | 1.80 | 2.16 | 0.45 |
| | Coker Distillate | 8.45 | 35.68 | 21.17 | 29.89 | 13.26 | 3.01 | 1.79 | 2.53 | 1.12 |
| RUN NO. 3125: | Pentane Soluble Fraction | 8.37 | 39.30 | 19.08 | 32.37 | 9.25 | 3.29 | 1.60 | 2.71 | 0.77 |
| | Benzene Soluble Fraction | 7.95 | 36.82 | 24.13 | 27.94 | 11.11 | 2.93 | 1.92 | 2.22 | 0.88 |
| | THF Soluble Fraction | 7.86 | 37.27 | 21.82 | 25.46 | 15.45 | 2.93 | 1.72 | 2.00 | 1.21 |
| | Coker Distillate | 8.60 | 35.34 | 21.55 | 30.18 | 12.93 | 3.04 | 1.85 | 2.60 | 1.11 |
| RUN NO. 3135: | Pentane Soluble Fraction | 8.36 | 34.83 | 24.72 | 29.21 | 11.24 | 2.91 | 2.07 | 2.44 | 0.94 |
| | Benzene Soluble Fraction | 7.94 | 36.11 | 25.00 | 27.78 | 11.11 | 2.87 | 1.98 | 2.21 | 0.88 |
| | THF Soluble Fraction | 7.88 | 35.03 | 26.75 | 27.39 | 10.83 | 2.76 | 2.11 | 2.16 | 0.85 |
| | Coker Distillate | 8.40 | 37.10 | 23.01 | 29.43 | 10.46 | 3.12 | 1.93 | 2.47 | 0.88 |

On the basis of our investigations molecular hydrogen has little effect on the conversion of coal to oil in conventional donor solvent liquefaction. The donor vehicle functions as the major external source of hydrogen for the stabilization of free-radicals. However, the limited degree of hydrogenation involving molecular hydrogen is most likely catalyzed by coal ash and/or sulphur constituents. These catalytic reactions may stabilize free-radicals directly or indirectly via a hydrogen donor mechanism.

## CONCLUSIONS AND RECOMMENDATIONS

Phase IV of our experimental studies on the direct hydroliquefaction of Nova Scotia coals has been completed. This phase of work was primarily concentrated on high pressure donor solvent liquefaction in a bench-scale continuous-flow unit. In addition, a catalyst screening program was carried out in a batch autoclave system to evaluate a number of potential coal hydrogenation catalysts.

During Phase IV twenty-four continuous donor solvent liquefaction experiments were carried out with Harbour and Hub seam coals from the Sydney Coalfield. The runs were made in a once-through mode of operation using hydrogenated anthracene oil, 9% H content, as the donor vehicle. As a result of this test program it was found that:

(a) Coal feedstock has a significant effect on product composition and hydrogen consumption.

(b) Temperature, over the range 440-460$^{o}$C, affects the conversion of coal to gases, oil, asphaltenes and preasphaltenes. In general, higher yields of gases and oil were observed at 460$^{o}$C.

(c) Pressure, over the range 17.24-20.68 MPa, had little effect on overall conversion. However, in the case of Prince mine coal hydrogen consumption was higher when operating at 20.68 MPa.

(d) Slurry feedrate, over the range 1-2 Kg/hr affected the yields of gases, oil and preasphaltenes. As expected, decreasing the

average residence time of coal in the reaction zone from 42 to 21 minutes resulted in lower gas and oil production and higher yields of preasphaltenes.

Hub seam coal from the Prince mine was found to be the most reactive feedstock at donor solvent liquefaction conditions. Within the Harbour seam reactivity was observed to decrease in going from the Lingan mine to No. 26. At high severity operating conditions coal conversions (THF solubles plus gases) ranged from 85-89% while oil yields ranged from 20-34%. The 34% oil yield was obtained from Prince coal whereas the No. 26 channel sample yielded only 20% product oil.

On completion of the continuous experiments simple correlations were drawn between individual coal parameters and product composition. The coal properties assessed were: pyritic sulphur, organic sulphur, total sulphur, carbon content, ash, vitrinite content and rank in terms of maximum reflectance of vitrinite. These correlations must be interpreted with caution, however, because in this series of tests several coal properties were interacting simultaneously to influence product yields. Nevertheless the correlations drawn suggest that:

(a) The presence of pyritic sulphur, organic sulphur and ash has a positive influence on coal conversion.

(b) Coals of higher carbon content give lower oil yields.

(c) Conversion of vitrinite is affected by other coal properties.

(d) Coals of lower rank, represented in terms of maximum vitrinite reflectance, give higher oil yields.

It has been demonstrated in the batch autoclave experiments that catalytic hydrogenation produces higher oil yields than donor solvent extraction. This is primarily attributed to the fact that the catalyst promotes chemical consumption of molecular hydrogen. In high severity experiments with Lingan coal and hydrogenated anthracene oil containing 7.6% H, oil yield was typically 25%. The addition of commercial Co/Mo and Ni/Mo hydrotreating catalysts, at the 5 wt. % level, increased oil yield to around 37%. The highest oil yield, 49%, was achieved using a catalyst mixture comprised of nickel chloride, ammonium molybdate and stannous chloride at a metals concentration of 0.75% based on dry coal.

In earlier phases of our experimental work efforts were focused on low severity (400$^{o}$C, <2100 kPa) donor solvent liquefaction. The main purpose of increasing severity at the extraction stage was to enhance liquid yield. The results of the testwork recently completed illustrate that although total conversion increased at high severity non-catalytic conditions, oil yield changed little. The reason being that the combination of donor solvent and molecular hydrogen, without catalyst, does not affect adequate transfer of hydrogen to the initial THF-soluble

products. Thus catalyst is required to stimulate and maintain hydrogenation reactions which are critical to the formation of product oil.

Based on our findings we recommend that experimental work be initiated on two-stage coal liquefaction. Two-stage liquefaction utilizes two separate, but closely coupled, reaction zones. The first-stage will be used to contain and control thermal dissolution reactions. The second-stage will contain and control catalytic hydrogenation and hydrofining reactions. By using this approach the dissolution step and the hydrogenation step can be separately optimized.

The objectives of two-stage liquefaction are as follows:

a) Higher liquid yields

b) Improved hydrogen utilization

c) Lower gas make

d) Better heteroatom removal

e) Minimum residuum production.

In our approach to two-stage liquefaction the first-stage will be operated at pressures of 3.45-6.89 MPa and temperatures of 425-460$^{o}$C. The second stage will function to stabilize the first-stage effluent while producing a recycle oil with high donor capacity. The catalytic second-stage will be operated at pressures of 17.24-20.68 MPa and temperatures of 370-405$^{o}$C.

All of our continuous experiments to date have been conducted in a once-through mode of operation. Thus we recommend that a series of continuous runs be made in a sequential format designed to generate a recycle oil from a Nova Scotia coal. It is recommended that the experiments be carried out using a commercial hydrotreating catalyst. This series of tests will serve to broaden our data base and provide a benchmark for two-stage liquefaction.

At present, conventional coal liquefaction is not commercially viable in Eastern Canada. Process developments are required to improve liquid yield and/or reduce capital costs. Two-stage direct hydroliquefaction offers the potential to enhance liquid yield and improve hydrogen utilization. Extensive testwork is required on two-stage processing schemes to determine the extent to which these improvements can be realized.

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# APPENDIX A

## CONVERSION CALCULATIONS

## APPENDIX A

### CONVERSION CALCULATIONS FOR CONTINUOUS COAL LIQUEFACTION EXPERIMENTS

Calculations are based on operations during the steady state sampling period.

### CONVERSIONS, WT. %:

$$\text{Pentane sol. + gases} = \frac{(\text{maf coal charged}) - (\text{organic pentane insol.})}{\text{maf coal charged}} \times 100$$

$$\text{Benzene sol. + gases} = \frac{(\text{maf coal charged}) - (\text{organic benzene insol.})}{\text{maf coal charged}} \times 100$$

$$\text{THF sol. + gases} = \frac{(\text{maf coal charged}) - (\text{organic THF insol.})}{\text{maf coal charged}} \times 100$$

$$\text{Gases} = \frac{\text{product gases}}{\text{maf coal charged}} \times 100$$

### DEFINITION OF PRODUCTS

Oil = pentane solubles

Asphaltenes = benzene solubles - pentane solubles

Preasphaltenes = THF solubles - benzene solubles

APPENDIX A

## CONVERSION CALCULATIONS FOR VACUUM DISTILLATION/COKING TESTS

Calculations are based on operations during the steady state sampling period.

$$\text{Distillate Yield, Wt. \%} = \frac{(\text{total distillate})^{*} - (\text{vehicle oil charged})}{\text{maf coal charged}} \times 100$$

*total distillate includes liquid recovered during vacuum distillation/coking operation plus light oil collected in the high pressure knock-out.

## CONVERSION CALCULATIONS FOR BATCH AUTOCLAVE CATALYST SCREENING TESTS

CONVERSIONS, WT. %:

$$\text{Benzene solubles plus gases} = \frac{(A-a) \times 10^{4}}{A(100-a)}$$

Where A = ash in benzene insoluble residue and a = ash in dry coal or dry coal-catalyst mixture, ashed at 750°C

$$\text{Gases} = \frac{\text{product gases}}{\text{maf coal charged}} \times 100$$

$$\text{Asphaltenes} = \frac{\text{asphaltenes precipitated}}{\text{maf coal charged}} \times 100$$

$$\text{Oil} = \text{benzene solubles} - \text{asphaltenes}$$

# APPENDIX B

## SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

APPENDIX B

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE
FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO.<br>COAL TESTED | | 3110<br>PRINCE<br>BATCH D | 3111<br>PRINCE<br>BATCH D | 3112<br>PRINCE<br>BATCH D | 3114<br>PRINCE<br>BATCH D |
|---|---|---|---|---|---|
| A. | OPERATING CONDITIONS | | | | |
| | Unit Back Pressure, MPa | 20.68 | 17.24 | 17.24 | 20.68 |
| | Temperatures, °C: | | | | |
| | Reactor (internal) | 440 | 460 | 440 | 440 |
| | Slurry Preheater (Average) | 200 | 200 | 200 | 200 |
| | Hot Separator | 249 | 254 | 251 | 262 |
| | Feedrates: | | | | |
| | Slurry, Kg/hr | 1.034 | 2.060 | 0.995 | 1.968 |
| | Coal, Kg/hr | 0.310 | 0.618 | 0.299 | 0.590 |
| | Hydrogen, L/hr | 252. | 462. | 270. | 492. |
| | Hydrogen Treatrate, Wt. % Dry Coal | 7.5 | 6.9 | 8.3 | 7.7 |
| | Hours on Stream | 5.92 | 6.00 | 6.00 | 6.05 |
| B. | CONVERSIONS OF maf COAL, WT. % | | | | |
| | Pentane Solubles plus Gases | 43.9 | 44.1 | 43.1 | 35.8 |
| | Benzene Solubles plus Gases | 71.1 | 69.2 | 71.3 | 64.4 |
| | THF Solubles plus Gases | 87.1 | 85.3 | 86.9 | 84.9 |
| C. | PRODUCT YIELDS ON maf COAL, WT. % | | | | |
| | $CH_4$ | 2.1 | 2.9 | 2.4 | 1.5 |
| | $C_2H_6$ | 1.7 | 2.6 | 2.2 | 1.4 |
| | $C_3H_8$ | 1.8 | 2.2 | 1.8 | 1.2 |
| | $C_4H_{10}$ | 1.6 | 2.1 | 2.3 | 1.6 |
| | CO | 0.3 | 0.4 | 0.3 | 0.3 |
| | $H_2S$ | 1.2 | 1.0 | 1.5 | 1.4 |
| | $H_2O$ | 1.1 | 2.1 | 1.6 | 1.1 |
| | Oil | 34.1 | 30.8 | 31.0 | 27.3 |
| | Asphaltenes | 27.2 | 25.1 | 28.2 | 28.6 |
| | Preasphaltenes | 16.0 | 16.1 | 15.6 | 20.5 |
| | Unreacted Coal | 12.9 | 14.7 | 13.1 | 15.1 |
| D. | $H_2$ CONSUMPTION, WT. % OF maf COAL | 1.6 | 1.3 | 1.3 | 1.6 |

APPENDIX B

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE
FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | | 3115 | 3116 | 3117 | 3118 |
|---|---|---|---|---|---|
| COAL TESTED | | PRINCE BATCH D | PRINCE BATCH D | PRINCE BATCH D | PRINCE BATCH D |
| A. | OPERATING CONDITIONS | | | | |
| | Unit Back Pressure, MPa | 20.68 | 17.24 | 17.24 | 20.68 |
| | Temperatures, °C: | | | | |
| | Reactor (Internal) | 460 | 440 | 460 | 460 |
| | Slurry Preheater (Average) | 200 | 200 | 200 | 200 |
| | Hot Separator | 251 | 249 | 252 | 248 |
| | Feedrates: | | | | |
| | Slurry, Kg/hr | 1.017 | 2.039 | 0.982 | 2.020 |
| | Coal, Kg/hr | 0.305 | 0.612 | 0.295 | 0.606 |
| | Hydrogen, L/hr | 246. | 504. | 252. | 504. |
| | Hydrogen Treatrate, Wt. % Dry Coal | 7.4 | 7.6 | 7.9 | 7.6 |
| | Hours on Stream | 6.05 | 6.05 | 6.23 | 7.00 |
| B. | CONVERSIONS OF maf COAL, WT. % | | | | |
| | Pentane Solubles plus Gases | 50.7 | 34.0 | 50.1 | 45.2 |
| | Benzene Solubles plus Gases | 76.5 | 63.8 | 75.7 | 70.4 |
| | THF Solubles plus Gases | 88.4 | 84.3 | 87.9 | 86.9 |
| C. | PRODUCT YIELDS ON maf COAL, WT. % | | | | |
| | $CH_4$ | 3.9 | 1.7 | 4.2 | 2.7 |
| | $C_2H_6$ | 3.4 | 1.4 | 3.8 | 2.4 |
| | $C_3H_8$ | 3.8 | 1.7 | 3.6 | 2.6 |
| | $C_4H_{10}$ | 2.6 | 1.5 | 3.4 | 2.0 |
| | CO | 0.5 | 0.2 | 0.4 | 0.4 |
| | $H_2S$ | 1.0 | 1.3 | 1.4 | 1.4 |
| | $H_2O$ | 2.5 | 1.5 | 3.6 | 1.4 |
| | Oil | 33.0 | 24.7 | 29.7 | 32.3 |
| | Asphaltenes | 25.8 | 29.8 | 25.6 | 25.2 |
| | Preasphaltenes | 11.9 | 20.5 | 12.2 | 16.5 |
| | Unreacted Coal | 11.6 | 15.7 | 12.1 | 13.1 |
| D. | $H_2$ CONSUMPTION, WT. % OF maf COAL | 2.0 | 1.1 | 1.7 | 1.6 |

APPENDIX B

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE
FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3119 | 3120 | 3122 | 3123 |
|---|---|---|---|---|
| COAL TESTED | PRINCE BATCH C | PRINCE BATCH C | LINGAN BATCH K | LINGAN BATCH K |
| **A. OPERATING CONDITIONS** | | | | |
| Unit Back Pressure, MPa | 17.24 | 17.24 | 20.68 | 17.24 |
| Temperatures, °C: | | | | |
| Reactor (Internal) | 460 | 450 | 460 | 460 |
| Slurry Preheater (Average) | 200 | 200 | 200 | 200 |
| Hot Separator | 251 | 249 | 251 | 251 |
| Feedrates: | | | | |
| Slurry, Kg/hr | 1.022 | 1.025 | 1.996 | 1.087 |
| Coal, Kg/hr | 0.307 | 0.308 | 0.599 | 0.326 |
| Hydrogen, L/hr | 246. | 246. | 492. | 246. |
| Hydrogen Treatrate, Wt. % Dry Coal | 7.4 | 7.4 | 7.5 | 6.9 |
| Hours on Stream | 6.12 | 6.02 | 6.05 | 6.00 |
| **B. CONVERSIONS OF maf COAL, WT. %** | | | | |
| Pentane Solubles plus Gases | 47.3 | 45.1 | 35.0 | 42.2 |
| Benzene Solubles plus Gases | 73.7 | 70.5 | 61.6 | 68.4 |
| THF Solubles plus Gases | 87.1 | 86.5 | 84.9 | 86.5 |
| **C. PRODUCT YIELDS ON maf COAL, WT. %** | | | | |
| $CH_4$ | 4.5 | 3.2 | 2.7 | 4.1 |
| $C_2H_6$ | 3.8 | 2.7 | 2.1 | 3.5 |
| $C_3H_8$ | 4.2 | 3.1 | 2.4 | 3.5 |
| $C_4H_{10}$ | 2.7 | 2.6 | 2.2 | 2.8 |
| CO | 0.4 | 0.3 | 0.3 | 0.4 |
| $H_2S$ | 0.9 | 0.9 | 0.4 | 0.5 |
| $H_2O$ | 3.5 | 2.8 | 1.2 | 1.2 |
| Oil | 27.3 | 29.5 | 23.7 | 26.2 |
| Asphaltenes | 26.4 | 25.4 | 26.6 | 26.2 |
| Preasphaltenes | 13.4 | 16.0 | 23.3 | 18.1 |
| Unreacted Coal | 12.9 | 13.5 | 15.1 | 13.5 |
| **D. $H_2$ CONSUMPTION, WT. % OF maf COAL** | 1.5 | 1.1 | 1.4 | 1.3 |

APPENDIX B

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE
FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. / COAL TESTED | | 3124 LINGAN BATCH K | 3125 LINGAN BATCH K | 3126 LINGAN BATCH K | 3127 LINGAN BATCH K |
|---|---|---|---|---|---|
| A. | OPERATING CONDITIONS | | | | |
| | Unit Back Pressure, MPa | 17.24 | 20.68 | 20.68 | 17.24 |
| | Temperatures, °C: | | | | |
| | Reactor (Internal) | 440 | 460 | 440 | 440 |
| | Slurry Preheater (Average) | 200 | 200 | 200 | 200 |
| | Hot Separator | 250 | 250 | 249 | 251 |
| | Feedrates: | | | | |
| | Slurry, Kg/hr | 1.984 | 1.038 | 2.020 | 1.042 |
| | Coal, Kg/hr | 0.595 | 0.311 | 0.606 | 0.313 |
| | Hydrogen, L/hr | 492. | 246. | 492. | 246. |
| | Hydrogen Treatrate, Wt. % Dry Coal | 7.5 | 7.2 | 7.4 | 7.2 |
| | Hours on Stream | 6.32 | 6.18 | 6.00 | 6.03 |
| B. | CONVERSIONS OF maf COAL, WT. % | | | | |
| | Pentane Solubles plus Gases | 24.8 | 41.0 | 24.2 | 33.0 |
| | Benzene Solubles plus Gases | 52.9 | 67.7 | 52.0 | 60.7 |
| | THF Solubles plus Gases | 81.9 | 87.1 | 83.2 | 85.8 |
| C. | PRODUCT YIELDS ON maf COAL, WT. % | | | | |
| | $CH_4$ | 1.7 | 3.9 | 1.5 | 2.2 |
| | $C_2H_6$ | 1.2 | 3.1 | 1.0 | 1.7 |
| | $C_3H_8$ | 1.0 | 3.0 | 0.9 | 1.4 |
| | $C_4H_{10}$ | 1.5 | 2.4 | 1.3 | 1.9 |
| | CO | 0.2 | 0.5 | 0.4 | 0.2 |
| | $H_2S$ | 0.6 | 0.5 | 0.5 | 0.5 |
| | $H_2O$ | 1.0 | 1.4 | 1.2 | 1.4 |
| | Oil | 17.6 | 26.2 | 17.4 | 23.7 |
| | Asphaltenes | 28.1 | 26.7 | 27.8 | 27.7 |
| | Preasphaltenes | 29.0 | 19.4 | 31.2 | 25.1 |
| | Unreacted Coal | 18.1 | 12.9 | 16.8 | 14.2 |
| D. | $H_2$ CONSUMPTION, WT. % OF maf COAL | 1.0 | 1.4 | 1.4 | 1.0 |

APPENDIX B

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE
FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3128 | 3129 | 3131 | 3132 |
|---|---|---|---|---|
| COAL TESTED | LINGAN BATCH K | LINGAN BATCH K | LINGAN BATCH J | LINGAN BATCH J |
| **A. OPERATING CONDITIONS** | | | | |
| Unit Back Pressure, MPa | 17.24 | 20.68 | 17.24 | 17.24 |
| Temperatures, °C: | | | | |
| Reactor (Internal) | 460 | 440 | 460 | 460 |
| Slurry Preheater (Average) | 200 | 200 | 200 | 200 |
| Hot Separator | 250 | 259 | 249 | 253 |
| Feedrates: | | | | |
| Slurry, Kg/hr | 2.045 | 1.005 | 1.029 | 1.007 |
| Coal, Kg/hr | 0.614 | 0.302 | 0.309 | 0.302 |
| Hydrogen, L/hr | 492. | 246. | 246. | 246. |
| Hydrogen Treatrate, Wt. % Dry Coal | 7.3 | 7.4 | 7.3 | 7.4 |
| Hours on Stream | 6.03 | 7.83 | 6.68 | 7.18 |
| **B. CONVERSIONS OF maf COAL, WT. %** | | | | |
| Pentane Solubles plus Gases | 35.5 | 30.0 | 47.0 | 45.1 |
| Benzene Solubles plus Gases | 60.8 | 59.9 | 71.7 | 71.3 |
| THF Solubles plus Gases | 85.5 | 85.7 | 89.4 | 88.9 |
| **C. PRODUCT YIELDS ON maf COAL, WT. %** | | | | |
| $CH_4$ | 2.8 | 2.2 | 4.2 | 4.7 |
| $C_2H_6$ | 2.2 | 1.8 | 3.8 | 3.9 |
| $C_3H_8$ | 2.2 | 1.5 | 3.5 | 3.6 |
| $C_4H_{10}$ | 2.1 | 1.8 | 2.8 | 3.1 |
| CO | 0.3 | 0.3 | 0.4 | 0.5 |
| $H_2S$ | 0.6 | 0.5 | 0.9 | 0.9 |
| $H_2O$ | 2.0 | 1.3 | 1.8 | 1.9 |
| Oil | 23.3 | 20.6 | 29.6 | 26.5 |
| Asphaltenes | 25.3 | 29.9 | 24.7 | 26.2 |
| Preasphaltenes | 24.7 | 25.8 | 17.7 | 17.6 |
| Unreacted Coal | 14.5 | 14.3 | 10.6 | 11.1 |
| **D. $H_2$ CONSUMPTION, WT. % OF maf COAL** | 1.4 | 1.4 | 1.8 | 1.5 |

APPENDIX B

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE
FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| | | | | | |
|---|---|---|---|---|---|
| RUN NO. | | 3133 | 3134 | 3135 | 3136 |
| COAL TESTED | | LINGAN BATCH 1 | LINGAN BATCH 1 | NO. 26 BATCH B | NO. 26 BATCH B |
| A. | OPERATING CONDITIONS | | | | |
| | Unit Back Pressure, MPa | 20.68 | 20.68 | 20.68 | 20.68 |
| | Temperatures, °C: | | | | |
| | Reactor (Internal) | 460 | 460 | 460 | 460 |
| | Slurry Preheater (Average) | 200 | 200 | 200 | 200 |
| | Hot Separator | 252 | 251 | 251 | 251 |
| | Feedrates: | | | | |
| | Slurry, Kg/hr | 1.072 | 1.005 | 1.031 | 0.995 |
| | Coal, Kg/hr | 0.322 | 0.302 | 0.309 | 0.299 |
| | Hydrogen, L/hr | 246. | 246. | 246. | 246. |
| | Hydrogen Treatrate, Wt. % Dry Coal | 7.0 | 7.4 | 7.2 | 7.5 |
| | Hours on Stream | 6.65 | 6.37 | 6.28 | 6.03 |
| B. | CONVERSIONS OF maf COAL, WT. % | | | | |
| | Pentane Solubles plus Gases | 41.8 | 44.0 | 36.3 | 37.0 |
| | Benzene Solubles plus Gases | 67.3 | 68.9 | 61.4 | 62.8 |
| | THF Solubles plus Gases | 87.0 | 87.7 | 85.1 | 85.7 |
| C. | PRODUCT YIELDS ON maf COAL, WT. % | | | | |
| | $CH_4$ | 4.2 | 4.2 | 4.2 | 4.4 |
| | $C_2H_6$ | 3.5 | 3.4 | 3.3 | 3.5 |
| | $C_3H_8$ | 3.0 | 3.2 | 2.9 | 3.1 |
| | $C_4H_{10}$ | 2.9 | 3.8 | 3.6 | 3.4 |
| | CO | 0.3 | 0.4 | 0.2 | 0.3 |
| | $H_2S$ | 0.4 | 0.3 | 0.0 | 0.0 |
| | $H_2O$ | 1.3 | 1.7 | 1.1 | 1.2 |
| | Oil | 26.2 | 27.0 | 21.0 | 21.1 |
| | Asphaltenes | 25.5 | 24.9 | 25.1 | 25.8 |
| | Preasphaltenes | 19.7 | 18.8 | 23.7 | 22.9 |
| | Unreacted Coal | 13.0 | 12.3 | 14.9 | 14.3 |
| C. | $H_2$ CONSUMPTION, WT. % OF maf COAL | 1.5 | 1.2 | 1.3 | 1.1 |

# APPENDIX C

## MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

APPENDIX C

## MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3110 | 3111 | 3112 | 3114 |
|---|---|---|---|---|
| COAL TESTED | PRINCE BATCH D | PRINCE BATCH D | PRINCE BATCH D | PRINCE BATCH D |
| MOISTURE, WT. % | 1.98 | 1.98 | 1.98 | 1.98 |
| ASH, WT. % DRY BASIS | 9.23 | 9.23 | 9.23 | 9.23 |
| HOURS ON STREAM | 5.92 | 6.00 | 6.00 | 6.05 |
| DURATION OF BALANCE PERIOD, HRS | 1.67 | 0.83 | 1.67 | 0.83 |
| INPUT (g): | | | | |
| $H_2O$ | 10.2 | 10.2 | 9.8 | 9.7 |
| Ash | 46.8 | 46.6 | 45.0 | 44.5 |
| maf Coal | 460. | 458. | 443. | 438 |
| Solvent | 1207. | 1202. | 1161. | 1148. |
| $H_2$ | 37.8 | 34.7 | 40.5 | 36.9 |
| Total | 1762. | 1752. | 1699. | 1677. |
| OUTPUT (g): | | | | |
| $H_2O$ | 15.2 | 19.9 | 16.9 | 14.7 |
| Ash | 39.4 | 44.2 | 38.7 | 39.7 |
| Organic THF Insolubles[1] | 59.5 | 67.3 | 58.0 | 66.1 |
| THF Solubles[2] | 1535. | 1530. | 1496. | 1520. |
| $H_2$ | 30.3 | 28.8 | 34.9 | 30.0 |
| Other Gases | 40.2 | 51.2 | 46.4 | 32.3 |
| Total | 1720. | 1741. | 1691. | 1703. |
| TOTAL MATERIAL RECOVERY, WT. % | 97.6 | 99.4 | 99.5 | 101.6 |

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes

APPENDIX C

## MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3115 | 3116 | 3117 | 3118 |
|---|---|---|---|---|
| COAL TESTED | PRINCE BATCH D | PRINCE BATCH D | PRINCE BATCH D | PRINCE BATCH D |
| MOISTURE, WT. % | 1.98 | 1.98 | 1.98 | 1.98 |
| ASH, WT. % DRY BASIS | 9.23 | 9.23 | 9.23 | 9.23 |
| HOURS ON STREAM | 6.05 | 6.05 | 6.23 | 7.00 |
| DURATION OF BALANCE PERIOD, HRS | 1.67 | 0.83 | 1.67 | 0.83 |
| INPUT (g): | | | | |
| $H_2O$ | 10.1 | 10.1 | 9.7 | 10.0 |
| Ash | 46.0 | 46.1 | 44.4 | 45.7 |
| maf Coal | 452. | 453. | 437. | 449. |
| Solvent | 1186. | 1189. | 1146. | 1178. |
| $H_2$ | 36.9 | 37.8 | 37.8 | 37.8 |
| Total | 1731. | 1736. | 1675. | 1721. |
| OUTPUT (g): | | | | |
| $H_2O$ | 21.5 | 16.7 | 25.3 | 16.5 |
| Ash | 41.4 | 42.6 | 40.9 | 42.7 |
| Organic THF Insolubles[1] | 52.4 | 71.1 | 53.0 | 58.6 |
| THF Solubles[2] | 1496. | 1506. | 1425. | 1490. |
| $H_2$ | 27.9 | 32.6 | 30.3 | 30.5 |
| Other Gases | 68.6 | 35.3 | 73.7 | 51.6 |
| Total | 1708. | 1704. | 1648. | 1690. |
| TOTAL MATERIAL RECOVERY, WT. % | 98.7 | 98.2 | 98.4 | 98.2 |

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes

APPENDIX C

## MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3119 | 3120 | 3122 | 3123 |
|---|---|---|---|---|
| COAL TESTED | PRINCE BATCH C | PRINCE BATCH C | LINGAN BATCH K | LINGAN BATCH K |
| MOISTURE, WT. % | 2.43 | 2.43 | 1.23 | 1.23 |
| ASH, WT. % DRY BASIS | 6.42 | 6.42 | 3.89 | 3.89 |
| HOURS ON STREAM | 6.12 | 6.02 | 6.05 | 6.00 |
| DURATION OF BALANCE PERIOD, HRS | 1.67 | 1.67 | 0.83 | 1.67 |
| INPUT (g): | | | | |
| $H_2O$ | 12.4 | 12.5 | 6.1 | 6.7 |
| Ash | 32.0 | 32.1 | 19.2 | 20.9 |
| maf Coal | 467. | 468. | 474. | 516. |
| Solvent | 1193. | 1196. | 1164. | 1268. |
| $H_2$ | 36.9 | 36.9 | 36.9 | 36.9 |
| Total | 1741. | 1746. | 1700. | 1849. |
| OUTPUT (g): | | | | |
| $H_2O$ | 28.9 | 25.8 | 11.8 | 15.7 |
| Ash | 27.4 | 27.7 | 16.7 | 15.7 |
| Organic THF Insolubles[1] | 60.1 | 63.0 | 71.7 | 69.6 |
| THF Solubles[2] | 1483. | 1502. | 1512. | 1596. |
| $H_2$ | 30.0 | 31.7 | 30.3 | 30.4 |
| Other Gases | 77.1 | 59.5 | 47.7 | 73.4 |
| Total | 1707. | 1710. | 1690. | 1801. |
| TOTAL MATERIAL RECOVERY, WT. % | 98.0 | 97.9 | 99.4 | 97.4 |

1 - Unreacted coal

2 - Oil, asphaltenes and preasphaltenes

APPENDIX C

## MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3124 | 3125 | 3126 | 3127 |
|---|---|---|---|---|
| COAL TESTED | LINGAN BATCH K | LINGAN BATCH K | LINGAN BATCH K | LINGAN BATCH K |
| MOISTURE, WT. % | 1.23 | 1.23 | 1.23 | 1.23 |
| ASH, WT. % DRY BASIS | 3.89 | 3.89 | 3.89 | 3.89 |
| HOURS ON STREAM | 6.32 | 6.18 | 6.00 | 6.03 |
| DURATION OF BALANCE PERIOD, HRS. | 0.83 | 1.67 | 0.83 | 1.67 |
| INPUT (g): | | | | |
| $H_2O$ | 6.1 | 6.4 | 6.2 | 6.4 |
| Ash | 19.1 | 19.9 | 19.4 | 20.0 |
| maf Coal | 471. | 493. | 479. | 494. |
| Solvent | 1157. | 1211. | 1178. | 1215. |
| $H_2$ | 36.9 | 36.9 | 36.9 | 36.9 |
| Total | 1690. | 1767. | 1720. | 1772. |
| OUTPUT (g): | | | | |
| $H_2O$ | 11.0 | 13.4 | 11.8 | 13.2 |
| Ash | 17.6 | 15.7 | 17.1 | 15.6 |
| Organic THF Insolubles[1] | 85.1 | 63.7 | 80.4 | 70.3 |
| THF Solubles[2] | 1491. | 1540. | 1521. | 1563. |
| $H_2$ | 32.1 | 29.8 | 30.1 | 31.9 |
| Other Gases | 28.9 | 66.1 | 27.0 | 39.2 |
| Total | 1666. | 1729. | 1687. | 1733. |
| TOTAL MATERIAL RECOVERY, WT. % | 98.6 | 97.8 | 98.1 | 97.8 |

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes

APPENDIX C

## MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3128 | 3129 | 3131 | 3132 |
|---|---|---|---|---|
| COAL TESTED | LINGAN BATCH K | LINGAN BATCH K | LINGAN BATCH J | LINGAN BATCH J |
| MOISTURE, WT. % | 1.23 | 1.23 | 1.47 | 1.47 |
| ASH, WT. % DRY BASIS | 3.89 | 3.89 | 6.37 | 6.37 |
| HOURS ON STREAM | 6.03 | 7.83 | 6.68 | 7.18 |
| DURATION OF BALANCE PERIOD, HRS | 0.83 | 1.67 | 1.67 | 1.25 |
| INPUT (g): | | | | |
| $H_2O$ | 6.3 | 6.2 | 7.6 | 5.6 |
| Ash | 19.6 | 19.3 | 32.3 | 23.7 |
| maf Coal | 485. | 477. | 474. | 348. |
| Solvent | 1193. | 1173. | 1200. | 881. |
| $H_2$ | 36.9 | 36.9 | 36.9 | 27.7 |
| Total | 1741. | 1712. | 1751. | 1286. |
| OUTPUT (g): | | | | |
| $H_2O$ | 15.9 | 12.1 | 16.3 | 12.3 |
| Ash | 18.0 | 16.1 | 25.1 | 20.8 |
| Organic THF Insolubles[1] | 70.3 | 67.5 | 50.1 | 38.7 |
| THF Solubles[2] | 1529. | 1514. | 1500. | 1145. |
| $H_2$ | 30.2 | 30.1 | 28.2 | 22.4 |
| Other Gases | 49.8 | 39.0 | 73.6 | 58.1 |
| Total | 1713. | 1679. | 1693. | 1297. |
| TOTAL MATERIAL RECOVERY, WT. % | 98.4 | 98.1 | 96.7 | 100.9 |

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes

APPENDIX C

## MATERIAL BALANCES FOR CONTINUOUS EXPERIMENTS USING NOVA SCOTIA COALS

| RUN NO. | 3133 | 3134 | 3135 | 3136 |
|---|---|---|---|---|
| COAL TESTED | LINGAN BATCH I | LINGAN BATCH I | NO. 26 BATCH B | NO. 26 BATCH B |
| MOISTURE, WT. % | 1.39 | 1.39 | 0.88 | 0.88 |
| ASH, WT. % DRY BASIS | 2.82 | 2.82 | 4.00 | 4.00 |
| HOURS ON STREAM | 6.65 | 6.37 | 6.28 | 6.03 |
| DURATION OF BALANCE PERIOD, HRS | 1.50 | 1.67 | 1.67 | 1.67 |
| INPUT (g): | | | | |
| $H_2O$ | 6.7 | 7.0 | 4.5 | 4.4 |
| Ash | 13.4 | 14.0 | 20.4 | 19.7 |
| maf Coal | 462. | 482. | 490. | 473. |
| Solvent | 1126. | 1173. | 1203. | 1161. |
| $H_2$ | 33.2 | 36.9 | 36.9 | 36.9 |
| Total | 1641 | 1713. | 1755. | 1695. |
| OUTPUT (g): | | | | |
| $H_2O$ | 12.4 | 14.9 | 9.9 | 9.7 |
| Ash | 10.9 | 12.3 | 17.3 | 16.3 |
| Organic THF Insolubles[1] | 59.9 | 59.5 | 73.1 | 67.7 |
| THF Solubles[2] | 1456. | 1502. | 1523. | 1477. |
| $H_2$ | 26.4 | 31.0 | 30.3 | 31.6 |
| Other Gases | 66.5 | 73.9 | 69.8 | 69.9 |
| Total | 1632. | 1694. | 1723. | 1672. |
| TOTAL MATERIAL RECOVERY, WT. % | 99.5 | 98.9 | 98.2 | 98.6 |

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes

# APPENDIX D

## ANALYSIS OF BENZENE-SOLUBLE FRACTIONS FROM CONTINUOUS COAL LIQUEFACTION TESTS

## ANALYSIS OF BENZENE-SOLUBLE FRACTIONS FROM CONTINUOUS COAL LIQUEFACTION TESTS

| RUN NO. | 3110 | 3112 | 3114 | 3116 | 3115 | 3117 | 3118 | 3111 |
|---|---|---|---|---|---|---|---|---|
| Carbon, Wt. % | 89.32 | 89.65 | 89.24 | 90.30 | 89.83 | 90.15 | 89.30 | 88.96 |
| Hydrogen, Wt. % | 8.27 | 8.08 | 7.97 | 8.30 | 7.83 | 7.75 | 7.98 | 8.01 |
| Nitrogen, Wt. % | 0.35 | 0.35 | 0.32 | 0.33 | 0.38 | 0.37 | 0.38 | 0.35 |
| Sulphur, Wt. % | 0.146 | 0.130 | 0.145 | 0.147 | 0.116 | 0.118 | 0.128 | 0.123 |
| Distillation Data, °C (by Gas Chromatography) | | | | | | | | |
| IBP/5 | | | 184/223 | 189/227 | 184/212 | 185/212 | | |
| 10/30 | | | 245/287 | 247/289 | 236/286 | 236/285 | | |
| 50 | | | 313 | 316 | 314 | 313 | | |
| 70/90 | | | 346/392 | 348/392 | 347/390 | 348/392 | | |
| 95/EP | | | 424/488 | 422/483 | 428/487 | 429/493 | | |

Prince Coal (Batch D) used for Run Nos. 3110-3118 inclusive.

## ANALYSIS OF BENZENE-SOLUBLE FRACTIONS FROM CONTINUOUS COAL LIQUEFACTION TESTS

| RUN NO. | 3129 | 3127 | 3126 | 3124 | 3125 | 3123 | 3122 | 3128 |
|---|---|---|---|---|---|---|---|---|
| Carbon, Wt. % | 90.30 | 89.29 | 89.63 | 89.95 | 90.00 | 90.87 | 90.57 | 89.39 |
| Hydrogen, Wt. % | 8.26 | 8.21 | 8.35 | 8.40 | 7.95 | 7.90 | 8.14 | 8.02 |
| Nitrogen, Wt. % | 0.37 | 0.37 | 0.33 | 0.33 | 0.41 | 0.39 | 0.37 | 0.36 |
| Sulphur, Wt. % | 0.060 | 0.061 | 0.059 | 0.058 | 0.051 | 0.050 | 0.056 | 0.054 |
| Distillation Data, °C (by Gas Chromatography) | | | | | | | | |
| IBP/5 | | | 190/226 | 189/227 | 181/211 | 183/211 | | |
| 10/30 | | | 247/289 | 247/289 | 234/284 | 234/284 | | |
| 50 | | | 314 | 315 | 313 | 313 | | |
| 70/90 | | | 346/390 | 347/391 | 347/393 | 347/391 | | |
| 95/EP | | | 422/501 | 421/488 | 431/494 | 429/492 | | |

Lingan Coal (Batch K) used for Run Nos. 3122-3129 inclusive.

## ANALYSIS OF BENZENE-SOLUBLE FRACTIONS FROM CONTINUOUS COAL LIQUEFACTION TESTS

| RUN NO. | 3119 | 3120 | 3131 | 3132 | 3133 | 3134 | 3135 | 3136 |
|---|---|---|---|---|---|---|---|---|
| COAL TESTED: | Prince Batch C | | Lingan Batch J | | Lingan Batch I | | No. 26 Batch B | |
| Carbon, Wt. % | 90.44 | 90.14 | 90.50 | 90.00 | 89.35 | 89.68 | 90.14 | 90.46 |
| Hydrogen, Wt. % | 7.72 | 7.76 | 7.99 | 7.96 | 7.87 | 7.86 | 7.94 | 7.96 |
| Nitrogen, Wt. % | 0.38 | 0.36 | 0.40 | 0.40 | 0.40 | 0.41 | 0.39 | 0.38 |
| Sulphur, Wt. % | 0.109 | 0.119 | 0.068 | 0.068 | 0.046 | 0.047 | 0.055 | 0.053 |
| Distillation Data, °C (by Gas Chromatography) | | | | | | | | |
| IBP/5 | | 184/213 | 179/210 | | | 181/211 | 184/212 | 177/208 |
| 10/30 | | 237/286 | 234/284 | | | 234/284 | 236/286 | 233/283 |
| 50 | | 314 | 313 | | | 313 | 314 | 313 |
| 70/90 | | 349/392 | 347/393 | | | 347/391 | 349/394 | 346/393 |
| 95/EP | | 424/483 | 431/487 | | | 428/487 | 432/488 | 434/497 |

# APPENDIX E

## STATISTICAL ANALYSIS OF $2^4$ FACTORIAL EXPERIMENT ON LINGAN AND PRINCE MINE COALS

APPENDIX E

RESPONSE FACTOR: GAS MAKE

| SLURRY FEEDRATE | 440°C | | | | 460°C | | | |
|---|---|---|---|---|---|---|---|---|
| | 17.24 MPa | | 20.68 MPa | | 17.24 MPa | | 20.68 MPa | |
| | P | L | P | L | P | L | P | L |
| 1 Kg/hr | 12.1 | 9.3 | 9.8 | 9.4 | 20.4 | 16.0 | 17.7 | 14.8 |
| 2 Kg/hr | 9.3 | 7.2 | 8.5 | 6.8 | 13.3 | 12.2 | 12.9 | 11.3 |

$\Sigma x = 191.0 \qquad C = \frac{(\Sigma x)^2}{n} = \frac{(191.0)^2}{16} = 2280.0625$

$SS_{Total} = \Sigma x^2 - C = 218.3775$

$SS_{Temperature} = 19,307.72/8 - C = 133.4025$

$SS_{Pressure} = 18,277.48/8 - C = 4.6225$

$SS_{Feedrate} = 18,632.50/8 - C = 49.0000$

$SS_{Coal} = 18,385.00/8 - C = 18.0625$

ANALYSIS OF VARIANCE

| SOURCE | df | SS | MS | F | CONFIDENCE LEVEL | EFFECT* |
|---|---|---|---|---|---|---|
| Temperature | 1 | 133.4025 | 133.4025 | 110.4143 | .99 | + 46.2 |
| Pressure | 1 | 4.6225 | 4.6225 | 3.8259 | .90 | - 8.6 |
| Feedrate | 1 | 49.0000 | 49.0000 | 40.5562 | .99 | - 28.0 |
| Coal | 1 | 18.0625 | 18.0625 | 14.9499 | .99 | - 17.0 |
| Residual | 11 | 13.2900 | 1.2082 | | | |
| Total | 15 | 218.3775 | | | | |

* n = 16

CALCULATION OF CONFIDENCE INTERVAL

$\Sigma x = 191.0$

$\bar{x} = \frac{\Sigma x}{n} = \frac{191.0}{16} = 11.9$

$s^2 = \frac{SS}{df} = \frac{13.2900}{11} = 1.2080$

$s = \sqrt{1.2080} = 1.10$

$s_{\bar{x}} = \frac{s}{\sqrt{n}} = \frac{1.10}{\sqrt{16}} = 0.3$

$\therefore$ the mean of 16 results at the $2\sigma$ confidence interval is:

$11.9 \pm 0.6$

APPENDIX E

RESPONSE FACTOR: OIL

| SLURRY FEEDRATE | 440°C | | | | 460°C | | | |
|---|---|---|---|---|---|---|---|---|
| | 17.24 MPa | | 20.68 MPa | | 17.24 MPa | | 20.68 MPa | |
| | P | L | P | L | P | L | P | L |
| 1 Kg/hr | 31.0 | 23.7 | 34.1 | 20.6 | 29.7 | 26.2 | 33.0 | 26.2 |
| 2 Kg/hr | 24.7 | 17.6 | 27.3 | 17.4 | 30.8 | 23.3 | 32.3 | 23.7 |

$\Sigma x = 421.6$ $\quad C = \frac{(\Sigma x)^2}{n} = \frac{(421.6)^2}{16} = 11{,}109.16$

$SS_{Total} = \Sigma x^2 - C = 409.0800$

$SS_{Temperature} = 89{,}288.00/8 - C = 51.8400$

$SS_{Pressure} = 88{,}902.16/8 - C = 3.6100$

$SS_{Feedrate} = 89{,}248.66/8 - C = 46.9225$

$SS_{Coal} = 90{,}934.10/8 - C = 257.6025$

ANALYSIS OF VARIANCE

| SOURCE | df | SS | MS | F | CONFIDENCE LEVEL | EFFECT* |
|---|---|---|---|---|---|---|
| Temperature | 1 | 51.8400 | 51.8400 | 11.6126 | .99 | + 28.8 |
| Pressure | 1 | 3.6100 | 3.6100 | 0.8087 | .75 | + 7.6 |
| Feedrate | 1 | 46.9225 | 46.9225 | 10.5111 | .99 | - 27.4 |
| Coal | 1 | 257.6025 | 257.6025 | 57.7054 | .99 | - 64.2 |
| Residual | 11 | 49.1050 | 4.4641 | | | |
| Total | 15 | 409.0800 | | | | |

*n = 16

CALCULATION OF CONFIDENCE INTERVAL

$\Sigma x = 421.6$

$\bar{x} = \frac{\Sigma x}{n} = \frac{421.6}{16} = 26.4$

$s^2 = \frac{SS}{df} = \frac{49.1050}{11} = 4.4641$

$s = \sqrt{4.4641} = 2.1$

$s_{\bar{x}} = \frac{s}{\sqrt{n}} = \frac{2.1}{\sqrt{16}} = 0.5$

$\therefore$ the mean of 16 results at the $2\sigma$ confidence interval is:

$26.4 \pm 1.0$

APPENDIX E

RESPONSE FACTOR: ASPHALTENES

| SLURRY FEEDRATE | 440°C | | | | 460°C | | | |
|---|---|---|---|---|---|---|---|---|
| | 17.24 MPa | | 20.68 MPa | | 17.24 MPa | | 20.68 MPa | |
| | P | L | P | L | P | L | P | L |
| 1 Kg/hr | 28.2 | 27.7 | 27.2 | 29.9 | 25.6 | 26.2 | 25.8 | 26.7 |
| 2 Kg/hr | 29.8 | 28.1 | 28.6 | 27.8 | 25.1 | 25.3 | 25.2 | 26.6 |

$\Sigma x = 433.8$ $\quad C = \frac{(\Sigma x)^2}{n} = \frac{(433.8)^2}{16} = 11{,}761.4025$

$SS_{Total} = \Sigma x^2 - C = 36.4575$

$SS_{Temperature} = 94{,}307.54/8 - C = 27.0400$

$SS_{Pressure} = 94{,}092.84/8 - C = 0.2025$

$SS_{Feedrate} = 94{,}091.54/8 - C = 0.0400$

$SS_{Coal} = 94{,}095.14/8 - C = 0.4900$

ANALYSIS OF VARIANCE

| SOURCE | df | SS | MS | F | CONFIDENCE LEVEL | EFFECT* |
|---|---|---|---|---|---|---|
| Temperature | 1 | 27.0400 | 27.0400 | 34.2495 | .99 | - 20.8 |
| Pressure | 1 | 0.2025 | 0.2025 | 0.2565 | .75 | + 1.8 |
| Feedrate | 1 | 0.0400 | 0.0400 | 0.0507 | .75 | - 0.8 |
| Coal | 1 | 0.4900 | 0.4900 | 0.6206 | .75 | + 2.8 |
| Residual | 11 | 8.6850 | 0.7895 | | | |
| Total | 15 | 36.4575 | | | | |

*n = 16

CALCULATION OF CONFIDENCE INTERVAL

$\Sigma x = 433.8$

$\bar{x} = \frac{\Sigma x}{n} = \frac{433.8}{16} = 27.1$

$s^2 = \frac{SS}{df} = \frac{8.6850}{11} = 0.7895$

$s = \sqrt{0.7895} = 0.9$

$s_{\bar{x}} = \frac{s}{\sqrt{n}} = \frac{0.9}{\sqrt{16}} = 0.2$

∴ the mean of 16 results at the 2σ confidence interval is:

$27.1 \pm 0.4$

APPENDIX E

RESPONSE FACTOR: PREASPHALTENES

| SLURRY FEEDRATE | 440°C | | | | 460°C | | | |
|---|---|---|---|---|---|---|---|---|
| | 17.24 MPa | | 20.68MPa | | 17.24 MPa | | 20.68 MPa | |
| | P | L | P | L | P | L | P | L |
| 1 Kg/hr | 15.6 | 25.1 | 16.0 | 25.8 | 12.2 | 18.1 | 11.9 | 19.4 |
| 2 Kg/hr | 20.5 | 29.0 | 20.5 | 31.2 | 16.1 | 24.7 | 16.5 | 23.3 |

$\Sigma x = 325.9 \qquad C = \frac{(\Sigma x)^2}{n} = \frac{(325.9)^2}{16} = 6638.1756$

$SS_{Total} = \Sigma x^2 - C = 490.6344$

$SS_{Temperature} = 53,966.53/8 - C = 107.6407$

$SS_{Pressure} = 53,110.85/8 - C = 0.6807$

$SS_{Feedrate} = 53,816.05/8 - C = 88.8307$

$SS_{Coal} = 55,370.05/8 - C = 283.0807$

ANALYSIS OF VARIANCE

| SOURCE | df | SS | MS | F | CONFIDENCE INTERVAL | EFFECT* |
|---|---|---|---|---|---|---|
| Temperature | 1 | 107.6407 | 107.6407 | 113.8332 | .99 | - 41.5 |
| Pressure | 1 | 0.6807 | 0.6807 | 0.7199 | .75 | + 3.3 |
| Feedrate | 1 | 88.8307 | 88.8307 | 93.9411 | .99 | + 37.7 |
| Coal | 1 | 283.0807 | 283.0807 | 299.3662 | .99 | + 67.3 |
| Residual | 11 | 10.4016 | 0.9456 | | | |
| Total | 15 | 490.6344 | | | | |

* n = 16

CALCULATION OF CONFIDENCE INTERVAL

$\Sigma x = 325.9$

$\bar{x} = \frac{\Sigma x}{n} = \frac{325.9}{16} = 20.4$

$s^2 = \frac{SS}{df} = \frac{10.4016}{11} = 0.9456$

$s = \sqrt{0.9456} = 1.0$

$s_{\bar{x}} = \frac{s}{\sqrt{n}} = \frac{1.0}{\sqrt{16}} = 0.3$

$\therefore$ the mean of 16 results at the 2$\sigma$ confidence interval is:

$20.4 \pm 0.6$

APPENDIX E

RESPONSE FACTOR: $H_2$ CONSUMPTION

| SLURRY FEEDRATE | 440°C | | | | 460°C | | | |
|---|---|---|---|---|---|---|---|---|
| | 17.24 MPa | | 20.68 MPa | | 17.24 MPa | | 20.68 MPa | |
| | P | L | P | L | P | L | P | L |
| 1 Kg/hr | 1.3 | 1.0 | 1.6 | 1.4 | 1.7 | 1.3 | 2.0 | 1.4 |
| 2 Kg/hr | 1.1 | 1.0 | 1.6 | 1.4 | 1.3 | 1.4 | 1.6 | 1.4 |

$\Sigma x = 22.5 \qquad C = \frac{(\Sigma x)^2}{n} = \frac{(22.5)^2}{16} = 31.6406$

$SS_{Total} = \Sigma x^2 - C = 1.0094$

$SS_{Temperature} = 254.57/8 - C = 0.1807$

$SS_{Pressure} = 255.77/8 - C = 0.3307$

$SS_{Feedrate} = 253.53/8 - C = 0.0507$

$SS_{Coal} = 254.93/8 - C = 0.2257$

ANALYSIS OF VARIANCE

| SOURCE | df | SS | MS | F | CONFIDENCE INTERVAL | EFFECT* |
|---|---|---|---|---|---|---|
| Temperature | 1 | 0.1807 | 0.1807 | 8.9900 | .95 | + 1.7 |
| Pressure | 1 | 0.3307 | 0.3307 | 16.4527 | .99 | + 2.3 |
| Feedrate | 1 | 0.0507 | 0.0507 | 2.5224 | .75 | - 0.9 |
| Coal | 1 | 0.2257 | 0.2257 | 11.2289 | .99 | - 1.9 |
| Residual | 11 | 0.2216 | 0.0201 | | | |
| Total | 15 | 1.0094 | | | | |

* n = 16

CALCULATION OF CONFIDENCE INTERVAL

$\Sigma x = 22.5$

$\bar{x} = \frac{\Sigma x}{n} = \frac{22.5}{16} = 1.4$

$s^2 = \frac{SS}{df} = \frac{0.2216}{11} = 0.0201$

$s = \sqrt{0.0201} = 0.14$

$s_{\bar{x}} = \frac{s}{\sqrt{n}} = \frac{0.14}{\sqrt{16}} = 0.04$

∴ the mean of 16 results at the 2σ confidence interval is:

$1.4 \pm 0.1$

# APPENDIX F

## PRELIMINARY RESULTS OF HPLC APPLIED TO COAL-DERIVED LIQUIDS

APPENDIX F

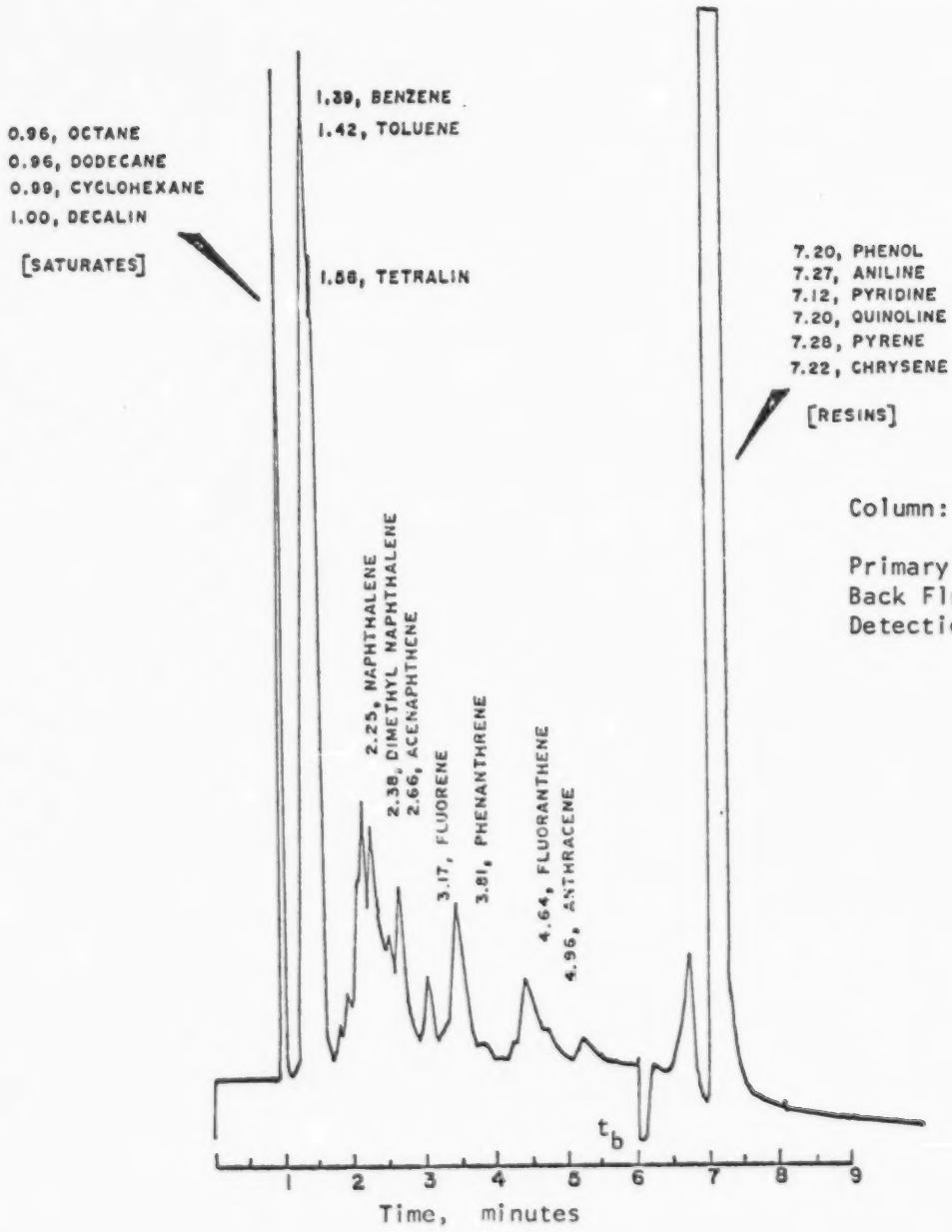
## PRELIMINARY RESULTS OF HPLC APPLIED TO COAL-DERIVED LIQUIDS

During Phase IV we acquired a Perkin-Elmer high performance liquid chromatographic system. The system is comprised of a Model 3B solvent delivery system, an LC-15 fixed wavelength UV detector (254 nm), and LC-25 refractometer detector, a solvent environmental chamber and pressurization system with helium degas and an automatic solvent switching valve. Analytical work relating to PONA (paraffins, olefins, naphthenes and aromatics) separation and GPC has been initiated. Results of preliminary work are presented in this section.

Figure 17 shows a typical HPLC separation of hydrogenated anthracene oil, 9% H, using a Perkin-Elmer analytical-scale amino-cyano column. This separation was achieved on a 5μL sample. Pentane was used as the mobile phase for six minutes in a forward operation then the column was backflushed with methyl-t-butyl ether. The solvent flowrate was 4 mL/minute. Forward eluting compounds were monitored by differential refractometry, while backflushed components were detected by the UV detector.

A number of model compounds have been used to define specific regions of the chromatogram. It has been established that saturates are eluted early and resins (polar aromatics and multi-ring compounds with four or more rings) are retained on the column until the backflush mode. The separation of aromatics and hydroaromatics appears to be based on the number of rings in a given molecule and the degree of

Figure 17 HPLC SEPARATION OF HYDROGENATED ANTHRACENE OIL

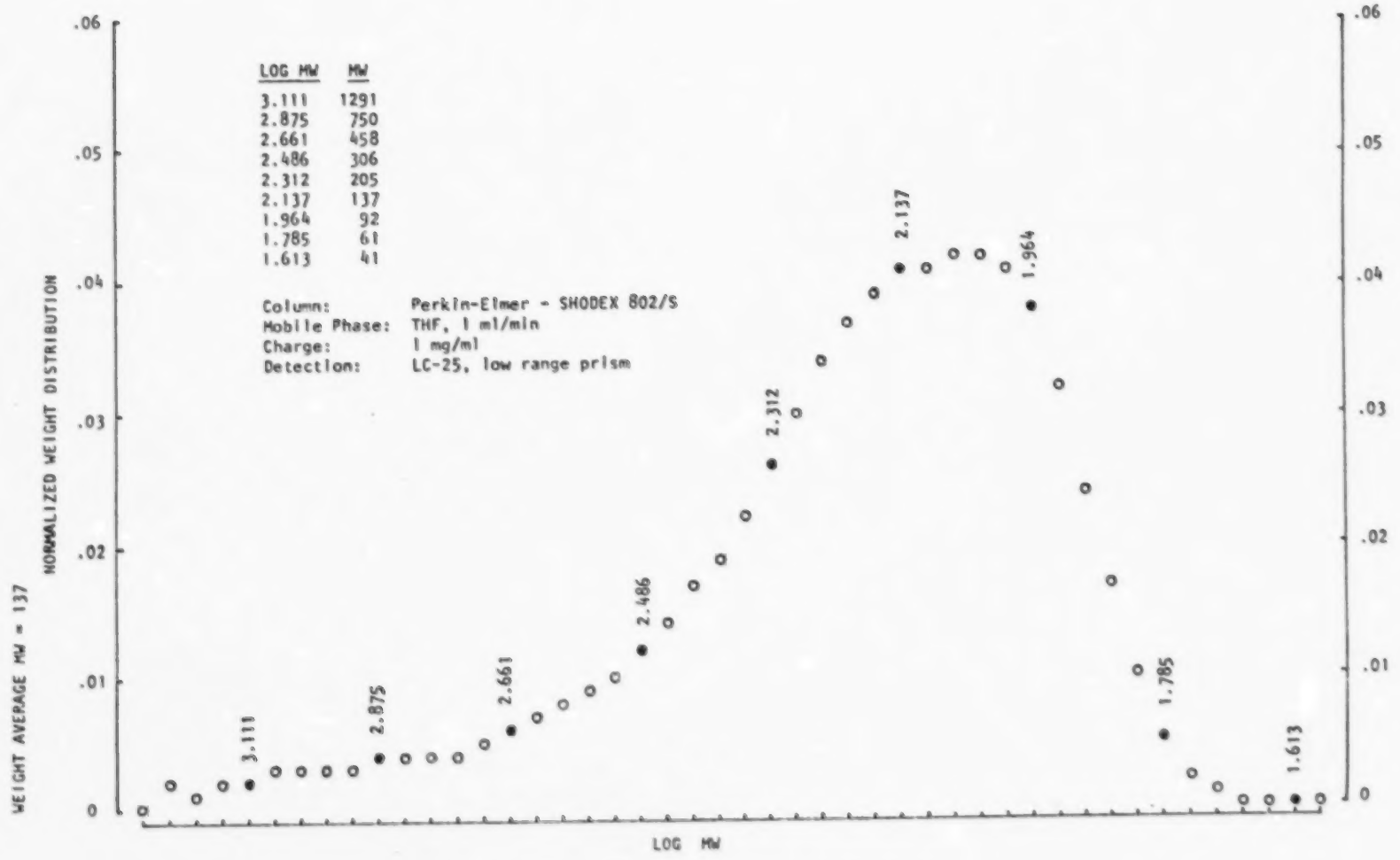



Column: Perkin-Elmer/Analytical amino-cyano
Primary Eluent: pentane, 4.0 ml/min.
Back Flush Solvent: methyl-t-butyl ether
Detection: LC-25, low range prism
LC-15, UV at 254 nm after $t_b$

unsaturation of the molecule. Attempts have been made to quantify the separation by collecting four effluent fractions. However, this is very difficult using an analytical column. In future we plan to investigate one or more columns and scale-up to a preparative operation. Once fractions can be collected quantitatively, detailed characterization is required to identify specific compound types.

Figures 18, 19 and 20 show typical GPC curves printed out by the Perkin-Elmer Sigma 10 chromatography data station. Molecular weight distributions are shown for hydrogenated anthracene oil and THF-soluble fractions from Run Nos. 3115 and 3116. This data was developed using a Perkin-Elmer SHODEX 802/S GPC column. Calibration was carried out using polystyrene standards. We are presently working on calibration using standard alkanes and aromatics. These GPC curves illustrate that in donor solvent liquefaction, higher severity operating conditions yield lower molecular weight products. In future, molecular weight studies will be carried out on oil, asphaltene and preasphaltene fractions isolated by solvent analysis and chromatographic methods.

Figure 18 - MOLECULAR WEIGHT DISTRIBUTION OF HYDROGENATED ANTHRACENE OIL BY GPC




F-5

Figure 19 - MOLECULAR WEIGHT DISTRIBUTION OF THF-SOLUBLE FRACTION FROM RUN NO. 3115 BY GPC

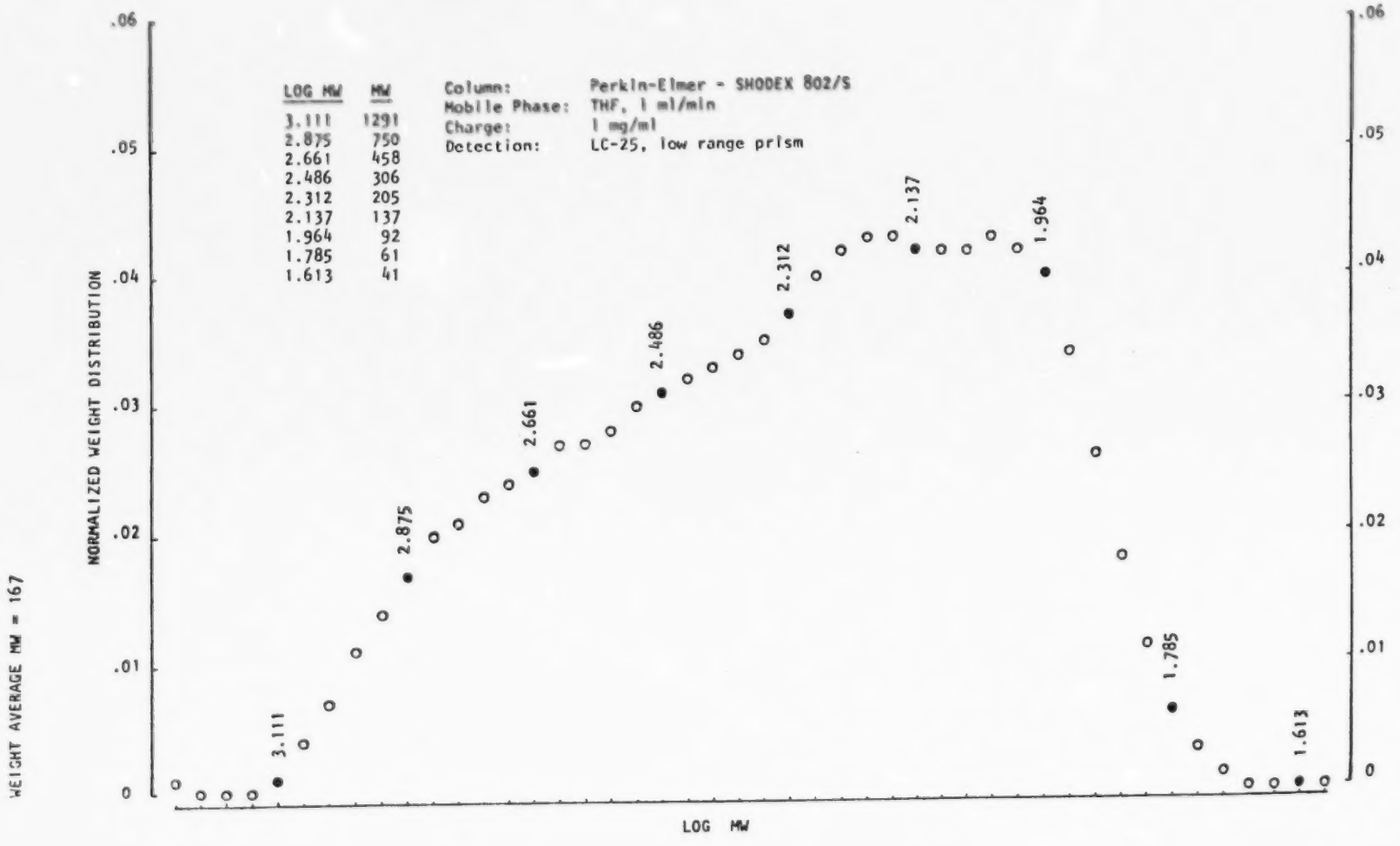
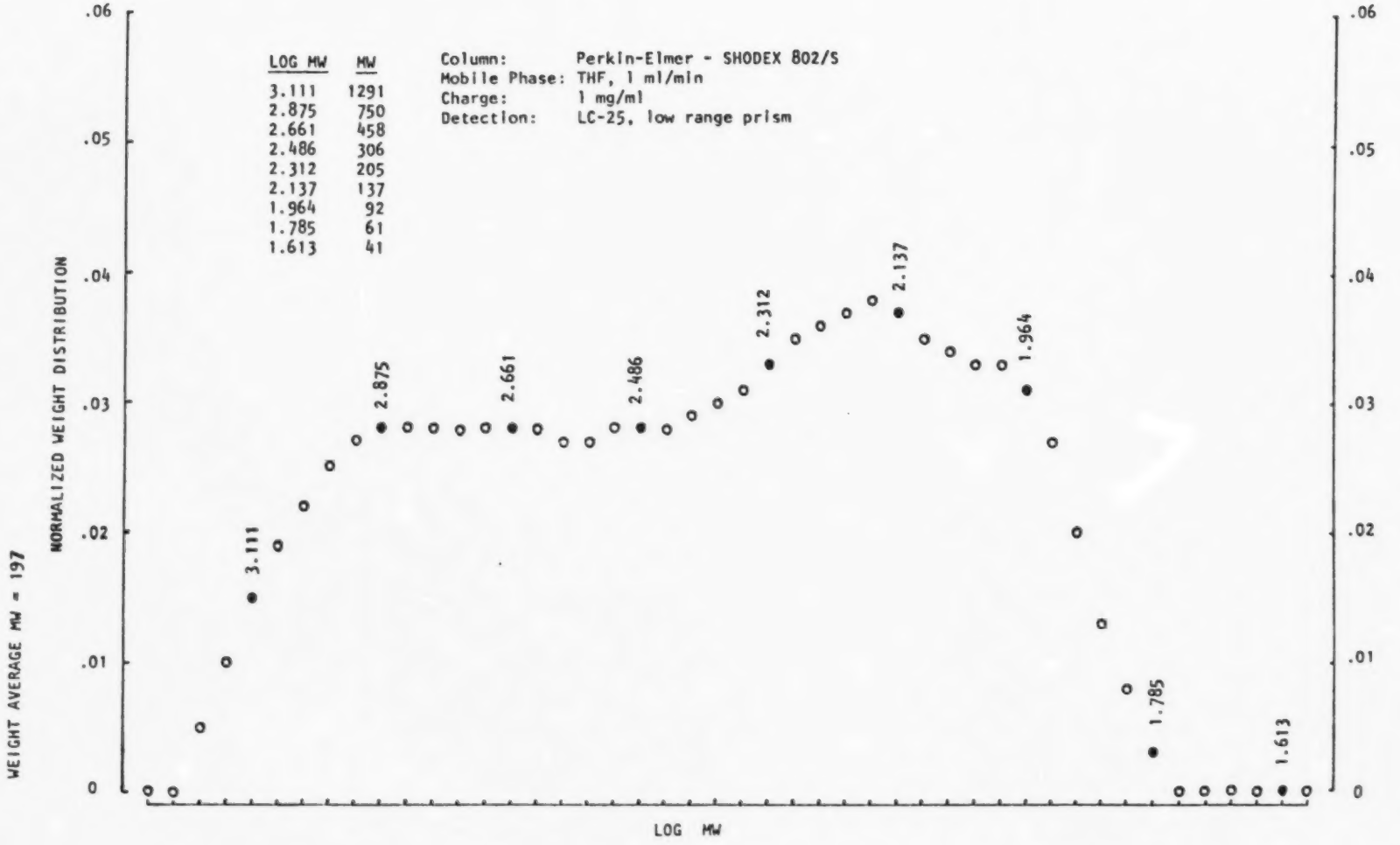


Figure 20 - MOLECULAR WEIGHT DISTRIBUTION OF THF-SOLUBLE FRACTION FROM RUN NO. 3116 BY GPC



# APPENDIX G

## OPERATING PROCEDURE FOR CONTINUOUS COAL LIQUEFACTION UNIT

## PREPARATION OF UNIT PRIOR TO ACTUAL OPERATION

This procedure is normally carried out the day before a run.

1. Prepare V-13 product withdrawal line for venting. All valves except Nos. 1, 103, 118 and 122 are closed.

2. Open valve Nos. 7, 20, 21, 24 and 25 to depressurize the system.

3. Prepare V-13 product withdrawal line for vacuum. Turn the vacuum pump on.

4. After one hour close valve Nos. 24 and 25 and then shut the vacuum pump off.

5. Open valve No. 2 and add hydrogen to 13.78 MPa, close valve No. 2. Leave for a few hours and observe for pressure leaks.

6. Set the forward pressure regulator and the back pressure regulator (B.P.R.) to the desired settings.

7. Add high pressure (H.P.) hydrogen to the system through valve No. 2 to 3.45 MPa less than the desired pressure, close valve No. 2.

8. Turn on the cooling water to the magnedrive stirrers.

9. Set the automatic timer to activate the STR furnace temperature controller at 5 hours prior to anticipated start-up.

## ACTUAL OPERATION

### Start-Up

1. Set the desired operating temperature on the furnace controller.

2. Turn the heating tapes on to the desired settings. Turn on the condenser cooling water.

3. Turn on the Hydrogen Flow Control System twenty minutes prior to run.

### Procedure

a) Turn on the power.
b) Open Valve No. 3.
c) Set the air pressure at 138 kPa.
d) Adjust the setpoint knob until the ball is in the center, then switch from manual to automatic.
e) Set the pen to the desired value.
f) Open valve No. 104 and close valve No. 103.
g) Allow the Hydrogen Flow Control System to stabilize.
h) Monitor exit gas flow readings for 15 minutes.

4. Charge V-1 with the slurry mixture. Open valve No. 101 and purge the feed tank with nitrogen. Open valve No. 102 and turn on the circulating pump.

5. When the temperature of the STR is at the desired level, purge the H.P. metering pump with slurry until the liquid is gas free.

Run

6. Open the plant valve (valve No. 5) and activate the H.P. metering pump.

7. Turn on the V-2 and V-3 magnedrive stirrers.

8. Monitor the pressures, temperatures, slurry feedrate and vent gas flowrates throughout the run.

9. Open valve No. 106 and 107 and purge V-6 with nitrogen, close valve No. 106 and 107.

10. After 1.8 Kg of slurry has been pumped, open valve Nos. 109, 110, 13 and 9.

11. Set the timers for the automatic letdown (ALD) system to maintain a constant level in V-3.

12. Activate the automatic letdown system.

13. Sample vent gas streams during the ALD period.

14. Drain liquid from the H.P. knock-out (V-13) periodically by opening and closing valve Nos. 24 and 25 sequentially.

15. Approximately one hour prior to steady state sampling period, close valve No. 9, open valve No. 8 and close valve No. 7 to transfer slurry product to V-4. Close valve No. 20.

16. Close valve Nos. 13, 109 and 110. Turn off the ALD system.

17. Open valve No. 117 to drain V-12, close valve No. 117.

18. Open valve No. 112. Manually withdraw slurry product from V-3 by opening valve Nos. 15 and 10, close valve Nos.10 and 15. After 15 minutes repeat this procedure. Close valve No.112.

19. Add H.P. hydrogen to V-3 by opening valve No. 22 until the pressure is 207 kPa greater than system pressure, close valve No. 22 and slowly open valve No. 20 to equalize system pressure.

20. To initiate steady state sampling period direct slurry product from V-4 to V-3. To do this open valve No. 7 and close valve No. 8. Close valve No. 21.

21. Repeat Step 17.

22. Open valve Nos. 114 and 115. Manually withdraw slurry product from V-4 by opening valve Nos. 18 and 17, close valve Nos. 17 and 18. After 15 minutes repeat this procedure. Close valve Nos. 114 and 115.

23. Add H.P. hydrogen to V-4 by opening valve No. 23 until the pressure is 207 kPa greater than system pressure, close valve No. 23. Slowly open valve No. 21 to equalize system pressure.

24. On completion of the steady state sampling period, open valve No. 8 and close valve No. 7 to redirect slurry product to V-4. Close valve No. 20.

25. Turn off the STR furnace temperature controller and the H.P. separator heaters. Reduce voltage to heating tapes on slurry transfer lines.

26. Shut off the Hydrogen Flow Control System.

Procedure

a) Turn the regulator knob until the ball is in the centre
b) Switch from automatic to manual
c) Shut off the air flow
d) Close valve No. 3
e) Turn off the power.

27. Deactivate the H.P. metering pump.

28. Close the plant valve (valve No. 5) and valve Nos. 8 and 21.

29. Transfer contents of V-2 into an evacuated H.P. vessel through valve No. 6. Leave valve No. 6 open for 1 hour.

30. Repeat step 17.

31. Open valve Nos. 119 and 120 and close valve No. 118 to bring the charcoal trap on-line.

32. Repeat step 18.

33. After one hour repeat step 17.

34. Open valve No. 118 and close valve Nos. 119 and 120. Remove the charcoal trap and weigh it.

35. Deactivate the circulating pump and drain slurry from the feed tank.

36. Open valve Nos. 20 and 21 to equalize the pressure.

37. Open valve No. 2 and add H.P. hydrogen to the STR until its pressure is 689 kPa in excess of the downstream pressure and then close valve No. 2.

38. Open valve No. 7 and equalize the pressure throughout the system. Open valve No. 103 and close valve No. 104.

Flush Cycle and Shut-Down

39. Reactivate the STR furnace temperature controller, the H.P. separator heaters and increase voltage to the heating tapes on slurry transfer lines to the desired settings.

40. Close valve No. 102, add flush oil to V-1, open valve No. 102 and turn on the circulating pump.

41. Purge the H.P. metering pump with oil until the liquid is gas free. Open the plant valve and activate the H.P. metering pump.

42. Turn off the condenser cooling water.

43. When 1.5 Kg of oil has been pumped into V-3 open valve Nos.109, 110, 13 and 9. Activate the ALD system allowing it to carry through 5 cycles, then close valve No. 9 and allow one more cycle. Deactivate the ALD system and close valve Nos. 109, 110 and 13.

44. Open valve No. 8 and close valve No. 7 to transfer oil to V-4. Close valve No. 20.

45. Withdraw oil from V-3. Slowly equalize pressure through valve No. 20.

46. After 1.5 Kg of oil has been pumped into V-4, open valve No. 7 and close valve No. 8 to transfer oil to V-3. Close valve No. 21.

47. Withdraw oil from V-4. Slowly equalize pressure through valve No. 21.

48. After 1.5 Kg of oil has been pumped into V-3, open valve No. 8 and close valve No. 7 to transfer oil to V-4. Close valve No. 20.

49. Withdraw oil from V-3. Slowly equalize pressure through valve No. 20.

50. After 1.5 Kg of oil has been pumped into V-4, deactivate the metering pump. Close the plant valve and valve Nos. 8 and 21.

51. Shut off all heating tapes, heaters and the STR furnace.

52. Transfer contents of V-2 into an evacuated H.P. vessel through valve No. 6. After 15 minutes close valve no. 6.

53. Turn off the magnedrive stirrer.

54. Drain flush oil from V-1.

55. Open valve Nos. 20 and 21 to equalize the pressure in V-3, V-4 and V-13.

## POST-RUN OPERATIONS

1. Open valve No. 2 and pressurize the STR to 10.34 MPa and then close valve No. 2.

2. Transfer contents of V-2 into an evacuated H.P. vessel through valve No. 6. After 15 minutes close valve No. 6.

3. Open valve No. 22 and pressurize V-3, V-4 and V-13 to 10.34 MPa and then close valve No. 22.

4. Close valve Nos. 20 and 21 and withdraw residual flush oil from V-3 and V-4.

5. Evacuate the system by following steps 1 to 5 on page G-2.

# APPENDIX H

## AUTOMATED HIGH PRESSURE LETDOWN SYSTEM

# AUTOMATED HIGH PRESSURE LETDOWN SYSTEM

## INTRODUCTION:

The electronic circuits for the Automated High Pressure Letdown System are designed to function with or without operational Gamma Ray Level Detection Equipment.

In the present application, Kay-Ray 4900F, Ion Chamber Level Switch, Model 7383 has been installed. The output circuit of this system consists of one double pole, double throw relay which signals the liquid level condition.

## Operational Procedure

### 1) Operation in conjunction with Gamma Ray Level Detection Equipment

Assume that the gamma ray system has been programmed so that when the designated liquid level in the vessel has been reached, the output relay of the instrument will energize, and will de-energize again when the liquid falls below that level.

### 1a) Operation with the Override Selector switch in the "Off" Position

When the designated level is reached, the gamma ray instrument output relay energizes:

The "Relay On" pilot light comes on
"A" valve opens for a period of time, selected on K1. The "A" valve pilot light comes on.
"A" valve closes. The light dims.
A pause follows, its duration is selected on K3.
"B" valve opens for the remainder of the discharge cycle. The "B" valve pilot light comes on.
"B" valve closes. The light dims.
The discharge cycle duration is selected on K2.
Under normal operating conditions the valve action will cause the liquid level in the vessel to fall as specified. This in turn will cause the gamma ray instrument output relay to de-energize after a period of time dependent upon the variable Time Constant of the gamma ray instrument.
The "Relay On" pilot light dims.
The "Relay Off" pilot light comes on.
When the liquid returns to the designated level the sequence will repeat itself.

If the liquid level in the vessel does not fall sufficiently, the gamma ray instrument output relay will remain energized. Under this condition after a period of time, selected on K6, the "High Level Alert" warning

lights will start to flash and the "High Level" front panel 115 Vac outlet will be powered intermittently for remote use.

If the liquid does not return to the designated level within a predetermined time as selected on K8, the "Low Level Alert" warning lights will start to flash and the "Low Level" front panel 115 Vac outlet will be powered intermittently for remote use.

1b) Operation with the Override Selector switch in the position "Automatic during High Alert"

Under normal conditions the operation proceeds as in 1a). If for some reason, inspite of the valve action the gamma ray instrument output relay does not de-energize, the system will automatically commence a series of discharge cycles after a period of time at a predetermined rate, selected on K6 and K5 respectively. The cycling will continue until the gamma ray instrument output relay de-energizes. Until such time the "High Alert" warning lights flash and the "High Alert" warning front panel 115 Vac outlet will be powered intermittently for remote use.

1c) Operation with the Override Selector switch in the position "Instantaneous/Continuous"

In the "Instantaneous/Continuous" override mode of operation the system will automatically maintain discharge cycles on a continuous basis at a predetermined rate, independent of the gamma ray instrument output relay power state. The rate is determined by the settings on K5.

Depending on the power state of the gamma ray instrument output relay, the "Relay energized" or "de-energized" pilot light will be lit and the High or Low Alert warning may flash.

2) Operation without Gamma Ray Level Detection Equipment

To operate, move the Override Selector switch to the "Instantaneous/Continuous" position. The system will automatically maintain discharge cycles on a continuous basis at a rate determined by the setting of K5 as in 1c) above.

The "Relay" and "Level Alert" pilot lights may or may not indicate during this mode of operation, however this is of no significance.

The sequence of operation is as follows:

"A" valve opens for a predetermined time as in 1a). The pilot light comes on.
"A" valve closes, the "A" valve pilot light dims.
Pause of preselected duration as in 1a).
"B" valve opens for remainder of cycle as in 1a). The "B" valve pilot light comes on.
"B" valve closes, the light dims.
The discharge cycle duration is as in 1a).
The cycle will repeat itself at a rate selected on K5 as in 1c).

NOTES:

1) Single Cycle Discharge

The "Single Cycle Discharge" switch when moved momentarily to the left or right will initiate a single discharge cycle independent of the gamma ray instrument output relay power state or mode of operation.

2) Provision for a Third Valve

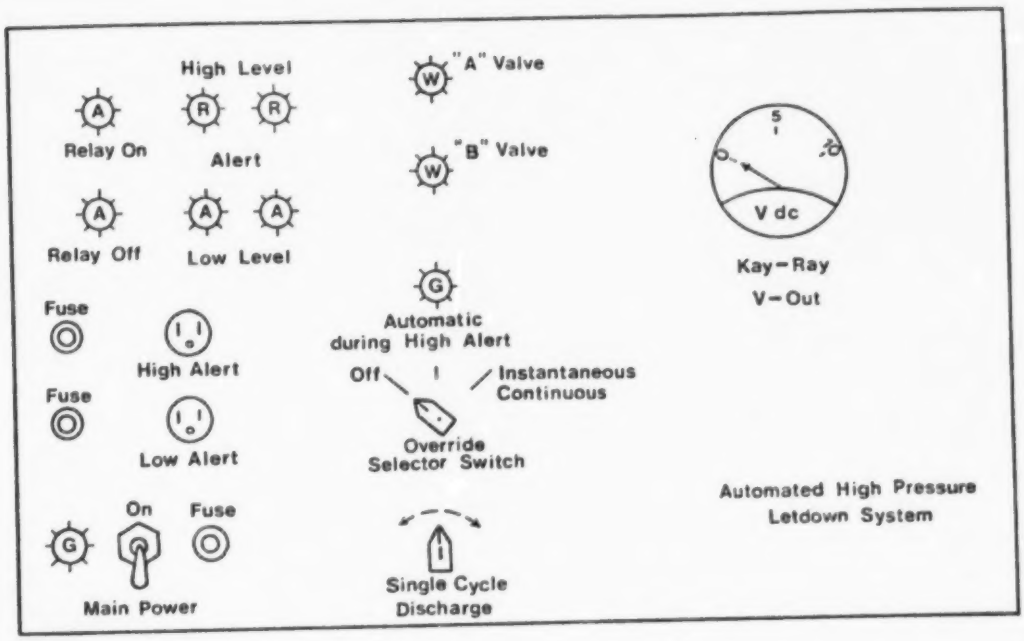
The electrical circuits provide for the installation of a third normally closed valve, the optional "C" valve. The overall sequence, including "C" is as follows. "A" valve opens; "A" valve closes; pause; "B" valve opens; pause, duration selected on K4; "C" valve opens; "B" and "C" valves close.

3) Valve Control

It should be noted that relays K1, 2, 3, and 4 are part of the valve controlling circuits. All four of these relays must be inserted in order for "A" valve to operate.

Also note that, electrically, valve "A" and "B" cannot be energized simultaneously. The purpose of variable time delay relay K3 is to introduce a pause after "A" valve closes before "B" can open in order to allow for a possible mechanical lag in the closing of "A" valve.

# AUTOMATED HIGH PRESSURE LETDOWN SYSTEM
## FRONT PANEL




### Legend

"Relay On"-Amber light signals Gamma Ray instrument output relay energized

"Relay Off"-Amber light signals Gamma Ray instrument output relay de-energized

"High Level Alert"-Red light flashing signals liquid remains at high level longer than selected time

"Low Level Alert"-Amber light flashing signals liquid remains at low level longer than selected time

"A" Valve-Clear light signals "A" valve open

"B" Valve-Clear light signals "B" valve open

High Alert Fuse-protects High Alert power outlet in parallel with High Alert Flashing lights

Low Alert Fuse-protects Low Alert power outlet in parallel with Low Alert Flashing lights

Use High Alert 115 Vac outlets for additional warning signals

Use Low Alert 115 Vac outlets for additional warning signals

Main Power Switch protected by Fuse. Green light signals power on

Override Selector Switch:

"Off" means no override function selected

"Automatic during High Alert" means Automatic discharge cycles governed by settings of K5 will proceed while "High Level Alert" lights are flashing. Green pilot light on.

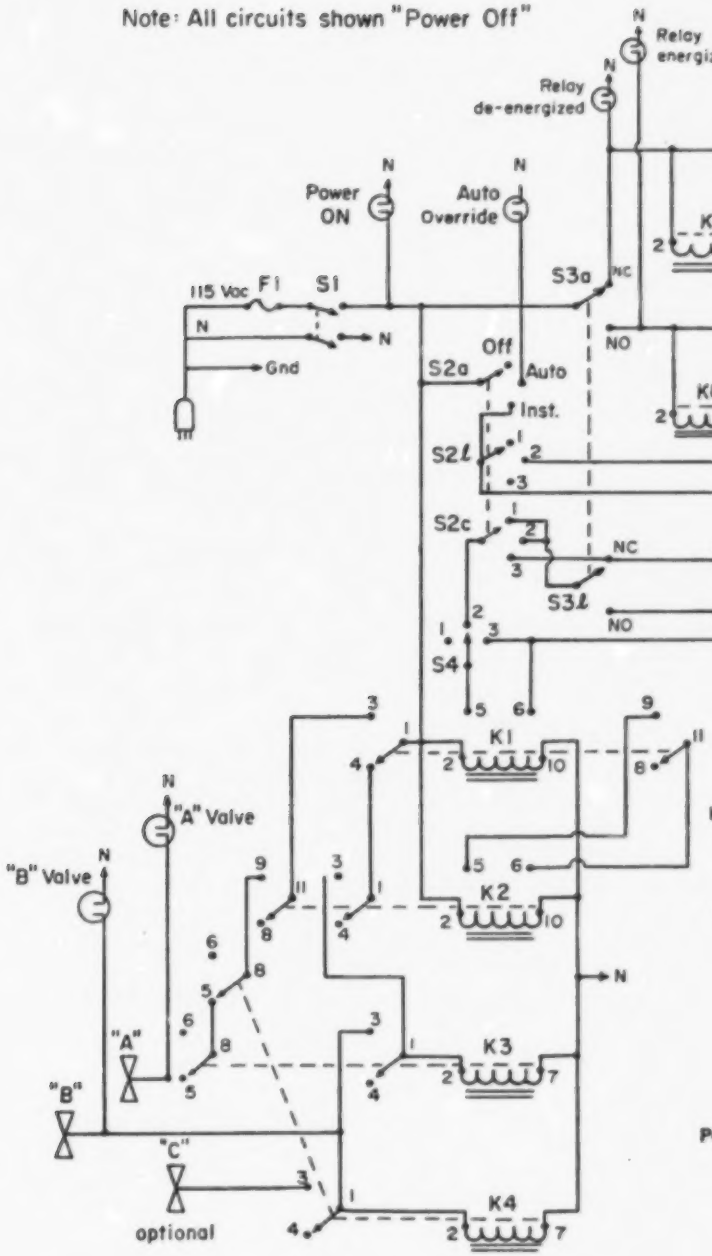
"Instantaneous/Continuous" means automatic discharge cycles will proceed continuously, independent of liquid level, based on settings of K5.

"Single Cycle Discharge"-When activated momentarily, a single discharge cycle will follow immediately, independent of mode of operation or liquid level.

"Kay-Ray V-Out"-Gamma-Ray instrument output relates to height of liquid level.

Automated High Pressure Letdown System
Front Panel Controls

NSRFC-07/27/83




F1; Fuse, 125V, 10A

F2,F3; Fuse, 125V, 1/2A

K1,K2; Timer Relay, "One Shot", 11 pin base

K3,K4,K6,K8; Timer Relay, "ON"-delay, 8 pin base

K5; Timer Relay, "ON/OFF", 8 pin base

K7,K9; Thermal-delay Relay, 8 pin base

Neon Lights; Clear, Amber, Red, Green, 125V

S1; DPST, Power On/Off Switch

S2; Rotary, Shorting, 3P3 Pos., Override Selector Switch.

S3; Gamma Ray Instrument, DPDT output relay contacts.

S4; SPDT, spring return, Single Cycle Discharge Switch.

Power Outlets; Standard dual wall, 125 V, 15A., modified.

Note: K1 controls duration of "A" valve open.

K2 controls duration of total discharge cycle (A open to B closed)

K3 controls delay before "B" valve opens after "A" closes.

K4 controls delay before "C" valve opens after "B" opens.

K5 controls intermission between discharge cycles on "Auto" and "Inst."

K6 controls delay before High level alert lights flash after S3 energizes.

K8 controls delay before Low level alert lights flash after S3 de-energizes.

NSRFC - 07/21/83

**Automated High Pressure Letdown System Circuit Diagram**

# APPENDIX I

## EQUIPMENT FOR CONTINUOUS COAL LIQUEFACTION UNIT

This section is included to provide more information on new equipment installed in the continuous coal liquefaction unit.

1. STIRRED TANK REACTOR

A double ended reactor constructed of 316 stainless steel, maximum allowable working pressure 35.5 MPa at 454°C. The reactor, 7.62 cm. diam. x 33.02 cm. long (internal dimensions) has a magnedrive stirrer complete with D.C. motor and variable speed controller. The autoclave is heated by a 2-zone split style hinged furnace. Autoclave Engineers Inc. (Erie, Pennsylvania) manufactured the reactor.

2. HYDROGEN FLOW CONTROL SYSTEM

Electronic D/P Cell Transmitter

A high pressure model with output signal of 4-20 mA DC and constructed of 316 stainless steel. The span limits are 20 to 205" $H_2O$. The transmitter is interfaced with a jewelled integral flow orifice of bore size 0.152 mm.

Electronic Recorder/Controller

Has an input of 4 - 20 mA, 105 to 125 Vac, 50 or 60 Hz, is single action, full proportional plus integral control, and a 21-103 kPa output signal.

Both of the above units were purchased from Foxboro Canada Ltd.

Research Control Valve

A pneumatic air-to-open valve constructed of 316 stainless steel. The trim is stellite with inner valve size of 0.0069 mm.

Also has a pneumatic positioner and a replacement stellite trim of size 0.0046 mm. The valve was manufactured by Badger Meter Inc., Research Control Valves, Tulsa, Oklahoma.

3) WEIGHED FEED SYSTEM

Includes a toledo scale consisting of a load cell of 25 Kg x .005 Kg capacity and a remote digital readout. The scale is available from Toledo Scale, a division of Reliance Electric Ltd., Windsor, Ontario.

4) TEMPERATURE CONTROLLERS

Provide control of the high temperature heating tapes on the high pressure separators. Have digital setpoint, analog indicator, 0 to 999 degrees C, proportional relay output and type K calibration. The controllers were purchased from Thermo Electric Canada Ltd., St. Laurent, Quebec.

5) BACK PRESSURE REGULATOR

Provides control of the system pressure. Has a maximum allowable working pressure of 34.5 MPa. The B.P.R. is available through Matheson of Canada Ltd., Whitby, Ontario.